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BRANDE'S  
MANUAL OF CHEMISTRY.

*SIXTH EDITION, GREATLY ENLARGED.*

IN TWO VOLUMES.

VOL. II.







A  
MANUAL  
OF  
CHEMISTRY.

BY

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&c., &c., &c.

VOLUME II.

CONTAINING

PART III. ORGANIC CHEMISTRY.

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LONDON:  
JOHN W. PARKER, WEST STRAND.

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## CHAPTER VII.

## ORGANIC CHEMISTRY.

ALTHOUGH the ultimate principles of organic substances are, comparatively speaking, few in number, yet by being combined under varying conditions, and in various proportions, they give rise to an innumerable series of products materially differing from each other, and which are called their *proximate components*. Carbon, hydrogen, oxygen, and nitrogen may be regarded as the principal ultimate elements of organized and organic products; sulphur and phosphorus are essential to some of them; and sodium, potassium, calcium, magnesium, and chlorine are also of frequent occurrence: silicium, fluorine, and manganese are likewise met with, and occasional traces of other substances. Of these, carbon and hydrogen may be considered as the most essential bases, and a numerous class of highly important products are constituted of those elements in combination with oxygen, so as to be empirically represented as oxides of hydrocarbons: nitrogen is also an eminently important constituent of several groups of organic products, and these azotised bodies are frequently associated with sulphur and phosphorus. The other substances are generally found in smaller and less definite proportions, and some of them appear in certain cases to be susceptible of mutual substitution. But it will be seen as we proceed, with how much caution we must reason as to the non-importance of certain organic elements, upon the mere ground of the small relative proportion in which they occur; the blood only contains about one-2000th of iron, yet without that iron, it would not be blood: in wheat flour there is not more than 1 part in 1000 of phosphorus, yet if destitute of phosphorus, it could not contribute to the formation of bone, brain, or nerve, and would therefore fall in the scale of nutritive importance.

The elements with which we shall most exclusively have to deal, in our examination of organic products, are carbon, hydrogen, oxygen, and nitrogen, and the number, and the varied characters, of the compounds to which they give rise under the influence of organization, is certainly most extraordinary; of this diversity, some of the causes will become apparent as we proceed; others have not only repulsed all attempts at explanation, but even baffle our most unlimited conjectures.

There is another leading distinction between *organic* and *inorganic* compounds, which is, that in the *latter* the elements may generally be represented as united in *binary* arrangements; thus, *crystallized sulphate of soda* is composed of sulphuric acid, soda, and water, which are *binary* compounds of sulphur and oxygen, sodium and oxygen, and hydrogen and oxygen; and this characteristic constitution of the products of inorganic chemistry will be found predominant even in the most complex combinations, numerous instances of which occur in the preceding pages.

But the products of organization are almost invariably of a *ternary* or *quaternary*, or even yet more complex character: thus *sugar* is constituted of carbon, hydrogen, and oxygen; *indigo* of carbon, oxygen,



hydrogen, and nitrogen; and *albumen* of carbon, hydrogen, oxygen, nitrogen, sulphur and phosphorus; and not this only, but each of these substances, regarded in its atomic relations, is made up of a number of single atomic components; the simplest view, for instance, which can be taken of the atom of sugar, represents it including 12 atoms of carbon, 9 of hydrogen, and 9 of oxygen: indigo is constituted of 16 atoms of carbon, 5 of hydrogen, 2 of oxygen, and 1 of nitrogen; and albumen has been represented by the highly complex formula of 400 atoms of carbon, 310 of hydrogen, 120 of oxygen, 50 of nitrogen, 2 of sulphur, and 1 of phosphorus. One obvious consequence of these atomic relations, is the high equivalent by which most organic bodies are necessarily represented; thus 222 parts of *quinia* are required to saturate 40 of sulphuric acid, and 132 of *tartaric acid* to saturate 32 of soda. Even as regards the simplest organic products, the hydrocarbons for instance, although containing two elements only, yet several atoms of each element go to form one compound atom: the atom of oil of turpentine (which is a binary compound of carbon and hydrogen) includes 10 atoms of carbon and 8 of hydrogen; and that of oil of lemons, 5 and 4, &c.

Cases of *isomerism* are of frequent occurrence in organic chemistry, and perhaps, strictly speaking, peculiar to organic products: such are some of the instances already cited (pp. 475, 507, &c.) They are sometimes referable to difference in the absolute number of simple atoms concerned in the production of a compound atom, and sometimes seem to depend upon peculiarities of atomic arrangement. The isomerism of binary compounds, as of the hydrocarbons, illustrates the former, and that of urea and cyanate of ammonia the latter: many other instances occur among organic compounds which remain to be described.

The instability which to a great extent characterizes organic products seems also in great measure to arise out of the above-mentioned peculiarities of their atomic constitutions; and accordingly we find that, under circumstances in which inorganic compounds remain invulnerable, organic substances are subject to a variety of mutations, the tendency of these being generally such as to terminate in the production of binary compounds. The complicated phenomena of fermentation, putrefaction, and decay, well illustrate these tendencies; and the very existence of organization is intimately dependent upon them: in these cases several intermediate stages are often passed through, but the principal ultimate results are *carbonic acid*, *water*, and *ammonia*; and it will be found that these form the chief food of vegetables; and, that absorbed either from the atmosphere or from the soil, they furnish carbon, hydrogen, oxygen, and nitrogen, again to be elaborated into "proximate organic principles" by the mechanism of the plant. It is only under such conditions that vegetables can assimilate the materials of which their fabrics are built up, and, in fact, so combine them, as to form the proximate components of the animal frame; while, on the other hand, the animal functions work in the opposite direction, and produce the above-mentioned binary compounds. Thus are the tendencies of the animal and vegetable kingdoms found to work in diametrically opposite directions: the former decomposing and destructive, the latter composing and regenerative. The bearings of chemistry upon agriculture and medicine, upon health and disease, and upon physiology in all its branches, will be obvious from

these considerations; and there are many other of the most important arts, the principles and practice of which are intimately interwoven with this department of chemical science.

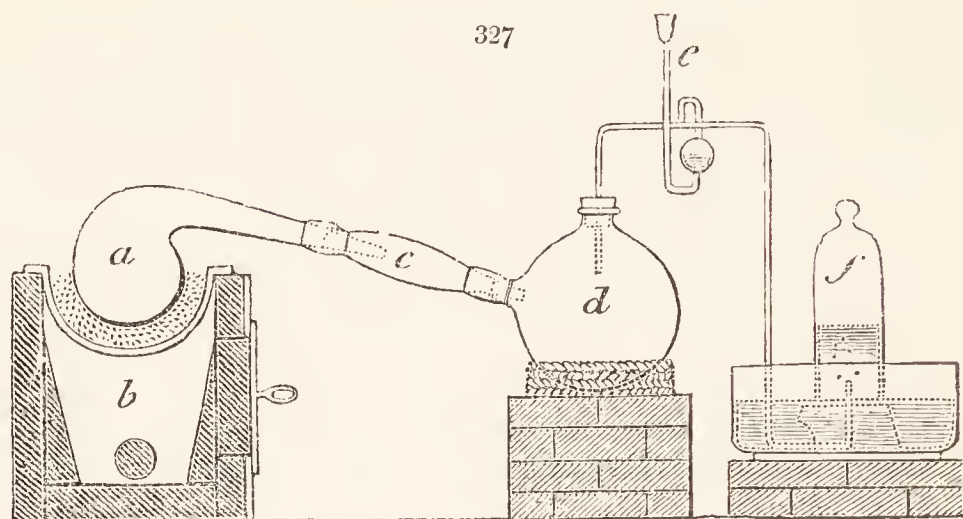
It has been impossible, in many previous discussions, and more especially in reference to the chemistry of *carbon*, to avoid a number of details, which, strictly speaking, are subjects of organic chemistry; and the history of the principal hydrocarbons, and of cyanogen, and their multifarious derivatives, have accordingly been postponed by some systematic writers to that branch of their subject; it is, however, obvious that no definite line can be drawn between organic and inorganic chemistry, or between the chemistry of compound and of simple radicals, founded upon the nature of the elements concerned, or the laws which preside over their mutual combination: any distinctions therefore to be made between those departments of the science must for the present be merely considered as matters of practical convenience calculated to facilitate the progress of the student; and that arrangement will be the least objectionable which is calculated to place in the most distinct points of view, the extremely complicated relations of the compounds of carbon presented in organic products, and their artificial derivatives. Under these circumstances, though I have much modified the classification of organic products adopted in former editions of this book, I have adhered to its principal subdivisions, and have not, for the reasons stated, attempted to draw a strict distinctive line between organic and inorganic chemistry, or to adopt the arrangements which have been founded upon the presumption of its existence. Where, as in these cases, *vitality* interferes, much must of necessity remain inexplicable, but the same general laws preside in all cases over the phenomena and results of chemical action.

## § I. OF THE ULTIMATE COMPOSITION AND ANALYSIS OF ORGANIC SUBSTANCES.

THE first attempts at the analysis of organic substances, consisted in subjecting them to *destructive distillation*, and this method was greatly extended and improved by Hales, Priestley, and the earlier pneumatic chemists, who paid especial attention to the gaseous products of such operations, which, together with aqueous and oily liquids, and a residue of carbon, constitute the general results of the process; hence the conclusion of the older chemists, that air, oil, water, and *earth*, including under that name the carbonaceous residue (or *caput mortuum*, as they called it), were the universal *elements* of organic bodies. It is, however, evident that most of these are secondary results, that they are *products* of the operation; and accordingly their composition and relative proportions are liable to infinite variation, dependent upon the manner in which the distillation has been effected. In modern analysis, therefore, this method is rejected, or at least only adopted where some specific product is to be examined, or where some general inference is to be drawn from the nature or proportions of the newly-produced compounds; *ammonia*, for instance, denotes the presence of nitrogen; a large quantity of *oil* announces excess of hydrogen; and of *acid* excess of *oxygen*; the uncondensed *gases*, and the residuary *carbon* may also be examined.



The following is one of the forms of apparatus in which these operations were usually carried on :—

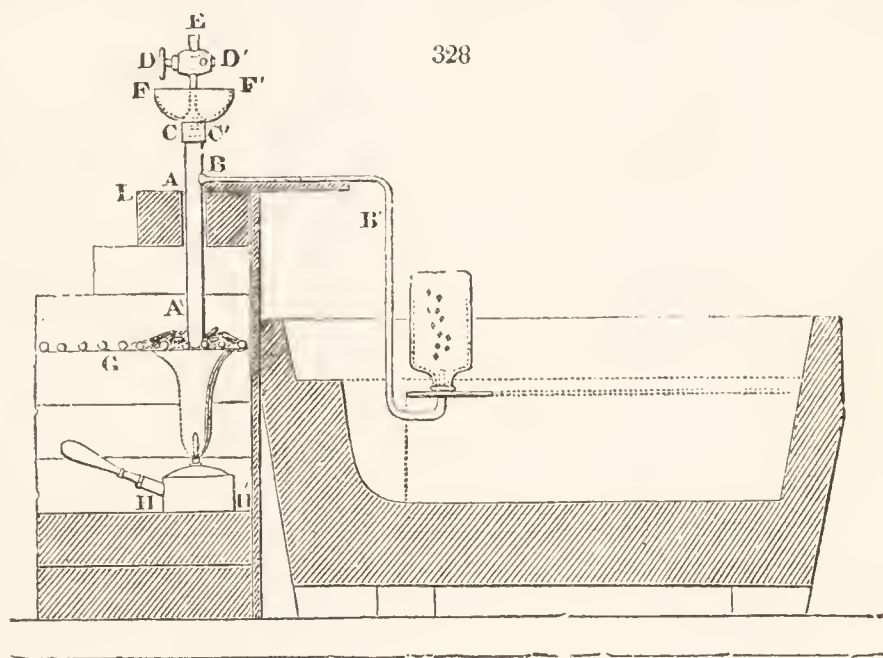


*a* is a luted glass or earthen retort, containing the substance to be decomposed, and placed in a sand-heat *b*, which is gradually raised to a red-heat. It is connected by the adapter *c* with the receiver *d*, which is kept cool for the condensation of the liquid products; the gases pass into the bell-glass *f* standing over water or mercury. *e* is a *tube of safety*, to allow for sudden expansion or contraction; there being in its lower part a small quantity of mercury which is occasionally elevated or depressed. The joints are secured by strips of moistened bladder.

If again we refer to the nature of the *ultimate elements* of organic bodies, it is obvious that combustion in oxygen will enable us to determine their relative proportions. To take the simplest instance, let us suppose the subject of analysis to consist of *carbon* and *hydrogen* only; in that case the products of its entire and perfect combustion in excess of oxygen would be *carbonic acid* and *water*; the quantity of *carbonic acid* being determined, that of the *carbon* which had formed it might be inferred; and this ascertained, and compared with the *original weight* of the substance, would give the proportion of *hydrogen*: thus, supposing 7 grains of the substance under examination yielded, by combustion in oxygen, 22 grains of carbonic acid, it would have consisted of 6 carbon + 1 hydrogen; for 22 carbonic acid (consisting of 6 carbon + 16 oxygen) are equivalent to 6 carbon. If the subject of analysis were a compound of carbon, hydrogen, and oxygen, the weight of the produced *water* would determine that of the hydrogen, and the deficiency would indicate that of the oxygen. Let us suppose 15 grains of a compound of carbon, hydrogen, and oxygen, to afford 22 grains of carbonic acid, and 9 of water; then we should again have 6 of carbon, and 1 of hydrogen, (for 9 of water = 1 hydrogen and 8 oxygen,) and there would be a deficiency of 8 grains, (required to make up the original 15,) which would be the inferred weight of the oxygen. When *nitrogen* is present, its quantitative determination requires other precautions to which I shall presently advert. So far, therefore, the mere *theory* of these ultimate analyses by combustion, is sufficiently simple; but the difficulties of *manipulation* are numerous and considerable; they relate, first, to the mode of effecting the *entire* combustion of the organic compound, and secondly, to the accurate collection and quantitative determination of the *products* of combustion.

Gay Lussac and Thenard (*Recherches Physico-Chimiques*, II.) were among the first who endeavoured to meet these difficulties, and to furnish accurate analyses upon the principles just stated. The method of effecting the combustion of an organic product in oxygen, which they originally adopted, consisted in forming a given weight of it into one or more pellets, with a requisite proportion of *chlorate of potassa*, and then subjecting them to a red-heat. An account of their process is given in THENARD'S *Traité de Chimie*, with the following arrangement and description of the apparatus. A hole is made through a brick L, and the

glass tube AA' is passed through it as far as to the small lateral tube BB', which passes into the mercurial trough. The lower extremity of the tube rests upon the grate G, where it is to be heated red-hot by charcoal inflamed by the lamp H. A brass cock is fitted, by grinding, to the tube cc'. It has a solid plug DD', in which is



a cavity large enough to contain one of the balls to be analysed, and which is introduced at the opening E. The plug is then turned round, and the ball falls into the red-hot part of the tube, where it burns, the gases passing into the mercurial apparatus. FF' is a basin, into which ice may be introduced to keep the metallic parts of the apparatus cool. It is convenient to case the lower part of the tube A in iron, as it is sometimes blown out at that part by the expansion within.

I shall not advert to the further proceedings with this apparatus, because it is rarely used. The chlorate of potassa is objectionable, because, except in particular cases, *perfect combustion* cannot be ensured by it; that is, the evolved gas is too suddenly generated, and is never perfectly *inodorous*; and in these analyses there should not be the smallest residuary vestige of the organic product appreciable by the empyreumatic smell of the produced carbonic acid or aqueous vapour.

To avoid the imperfections of this method, Gay Lussac afterwards suggested the employment of *oxide of copper* as a source of oxygen for the combustion; it has the advantage of resisting decomposition when heated alone, whilst it readily yields oxygen to carbon and hydrogen, at high temperatures. The analysis, therefore, as thus practised, consists in mixing the organic matter in due proportion with oxide of copper, and so subjecting it to combustion, that the carbon may be entirely converted into *carbonic acid*, and the hydrogen into *water*. When nitrogen is present it is collected in the state of *gas*, and the proportion of oxygen is estimated by the deficiency in the joint weights of the carbon, hydrogen, and nitrogen, as compared with the original weight of the portion of the organic product subjected to analysis.

The oxide of copper best adapted to this particular purpose is



obtained by heating copper-shavings to redness, exposed to air, and then bruising them in a mortar, by which the oxide is separated, and may be sifted off; or thin plates of copper may be successively quenched in water, when the scales of oxide fall off, and may be dried, powdered, and heated to redness in an open vessel. The oxide derived from the ignition of nitrate of copper is however preferable, as being finer and lighter than the preceding: it is obtained by calcining the nitrate in an earthen crucible at a dull red-heat, till fumes cease to be evolved, and no green particles remain: it should be stirred during the process with an iron rod; and as this oxide is *hygrometric*, it should be kept in stopped phials, and used warm, with as little exposure to air as possible.

Dr. Prout, to whom organic chemistry is deeply indebted for many excellent analyses, published a paper on this subject in the *Philosophical Transactions* for 1827, in which another form of apparatus was employed. Dr. Prout's object was, effectually to burn the organic substance in a given volume of pure gaseous oxygen; in which case, supposing it to contain three elements, hydrogen, carbon, and oxygen, one of three things happens. 1. The original bulk of the oxygen gas *remains the same*, in which case *the hydrogen and oxygen in the substance exist in it in the same proportions in which they exist in water*; or, 2. The original bulk of the oxygen is *increased*, in which case the oxygen exists in the substance in a *greater* proportion than it exists in water; or, 3. The original bulk of the oxygen is *diminished*, in which case the *hydrogen predominates*.

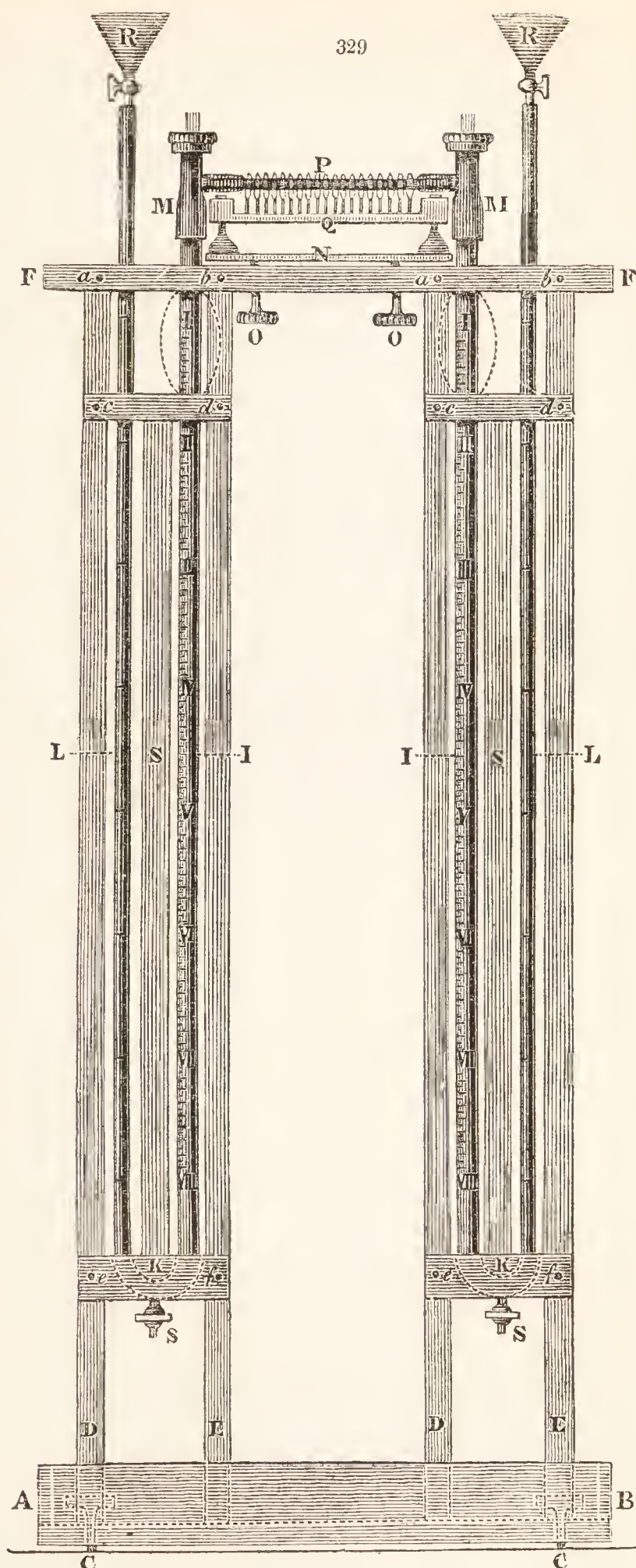
Hence, in the first of these cases, the composition of a substance may be determined by ascertaining the quantity of *carbonic acid gas* yielded by a known quantity of it; while in the other two, the same can be readily ascertained by the same data, and by noting the excess or diminution of the original bulk of the oxygen.

Fig. 329 represents a front view of Dr. Prout's apparatus for the determination of these points. AB is a platform, two feet square, surrounded by a ledge for preserving any mercury that may fall about, and furnished with four adjusting screws (of two of which cc are sectional views). Into this platform are fixed perpendicularly four pillars, DE, DE, about four feet and a half high, supporting another small platform, FF, about four inches wide, and which may be fixed or removed at pleasure by the brass pins, *a b*, *a b*. II are glass tubes, graduated to hundredths of a cubic inch, and cemented at bottom into semicircular iron tubes enclosed in the blocks KK (as represented by the dotted lines). These iron tubes project a little below the wood at the lower part, where they are furnished with iron stop-cocks, ss, for drawing off the mercury when it may be necessary. Into the other end of these semicircular tubes are likewise cemented the glass tubes, LL (of smaller dimensions, and a little longer than the tubes II), and forming with them, when taken together, inverted siphons. The smaller tubes, LL, are surmounted by funnels, RR, furnished with stop-cocks, the object of which is to permit the mercury to flow into them with any velocity that may be required. On the tops of the larger tubes, II, are cemented the vertical stop-cocks, MM, of which fig. 330 is a sectional view on a larger scale, and which renders the construction so obvious, that perhaps no further remark is necessary, than merely stating that the cup *a* is filled with oil, and that the plug *b*, which is square at the upper part, and adapted to a key, is furnished with a



shoulder, on which the screw-cap, *c*, rests, and by means of which it may be tightened at pleasure\*.

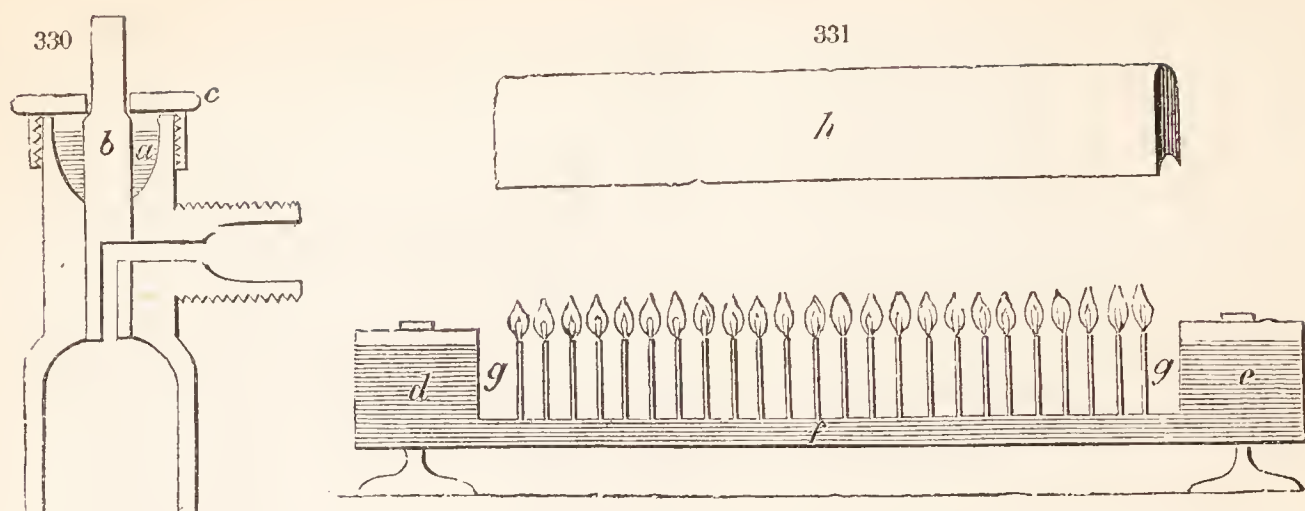
On the platform, *FF* (fig. 329), is a thin piece of wood, *N*, capable of being raised or depressed by the screws, *oo*; on this the lamp, *q*, is placed, at any distance that may be required from the tube *P*. Fig. 331 is an enlarged view of this lamp; it consists of two reservoirs, *d e*, for holding the spirit, connected together by means of the tube, *f*, into which are placed, at the distance from one another of about  $\frac{1}{3}$  of an inch, a number of vertical burners, *g g*, about one-twelfth of an inch in diameter, and  $\frac{3}{4}$  of an inch long, and *made as thin* as possible, with the view of preventing the conduction of the heat. These burners are each furnished with a few threads of cotton, and are bent a little alternately like the teeth of a saw, in order that their flame may envelop the tube *P* (fig. 329) more completely: *h* is a cover for the wick of the lamp when not in use. The tube *P* (fig. 329) is of green or bottle glass, moderately stout, and about one-fifth of an inch internal diameter. It is fixed between the horizontal



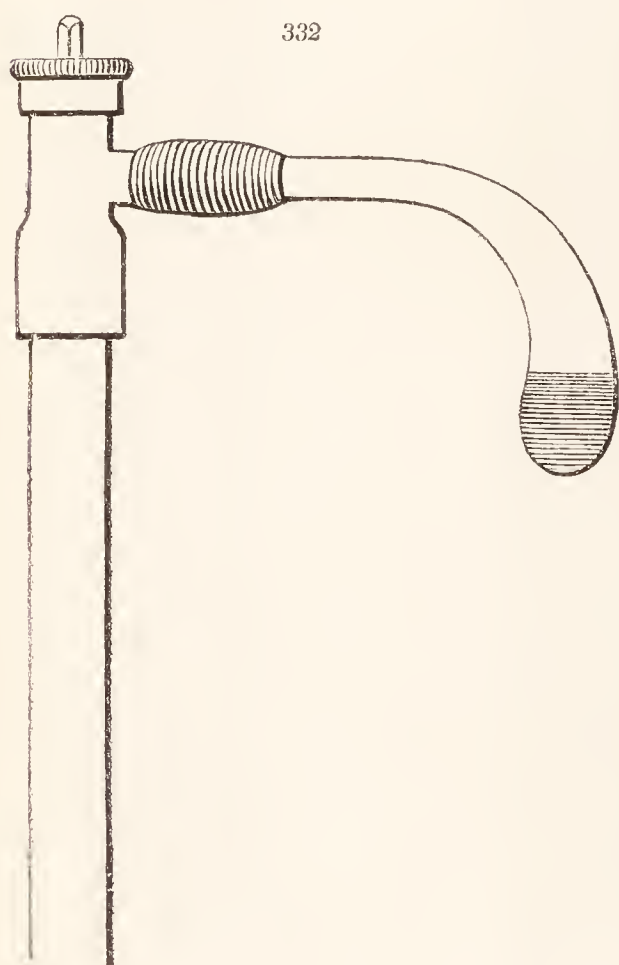
\* The siphons are fixed together independently of the general frame-work, and may be removed at pleasure by taking out the pins *cd*, *cd*, and *ef*, *ef*. This admits of their being replaced by others of different sizes. Those of a larger size have balls near the top, as represented by the dotted lines, and may contain as much as

20 cubic inches of gas. It much facilitates the process of determining the exact quantity of gas contained in the apparatus, to have both legs of the siphon graduated, which may be easily done so as to obviate the effects of capillary attraction when the tubes are not both of the same calibre.





parts of the vertical cocks, *MM*, so as to be perfectly air-tight; and when required, the whole, or any part of it, may be heated by means of the lamp *Q*, at the pleasure of the operator.



When the apparatus is to be employed, both the siphon-gasometers, *IL*, *IL*, are to be filled with quicksilver, and a small green-glass retort, containing the requisite quantity of chlorate of potassa (previously heated so as to expel the common air, and fill it with oxygen) is to be attached to one of the cocks, as represented in fig. 332, by means of a caoutchouc tube. Heat is then to be applied, and any quantity of oxygen gas that may be required, introduced into the tube *I*. After the whole has acquired the temperature of the atmosphere, the exact quantity of the gas is to be accurately noticed, as well as the state of the barometer and thermometer at the time. The tube *P*, containing the substance to be analyzed, is then to be firmly fixed between the cocks, *MM*\*, and subjected to heat, during which the

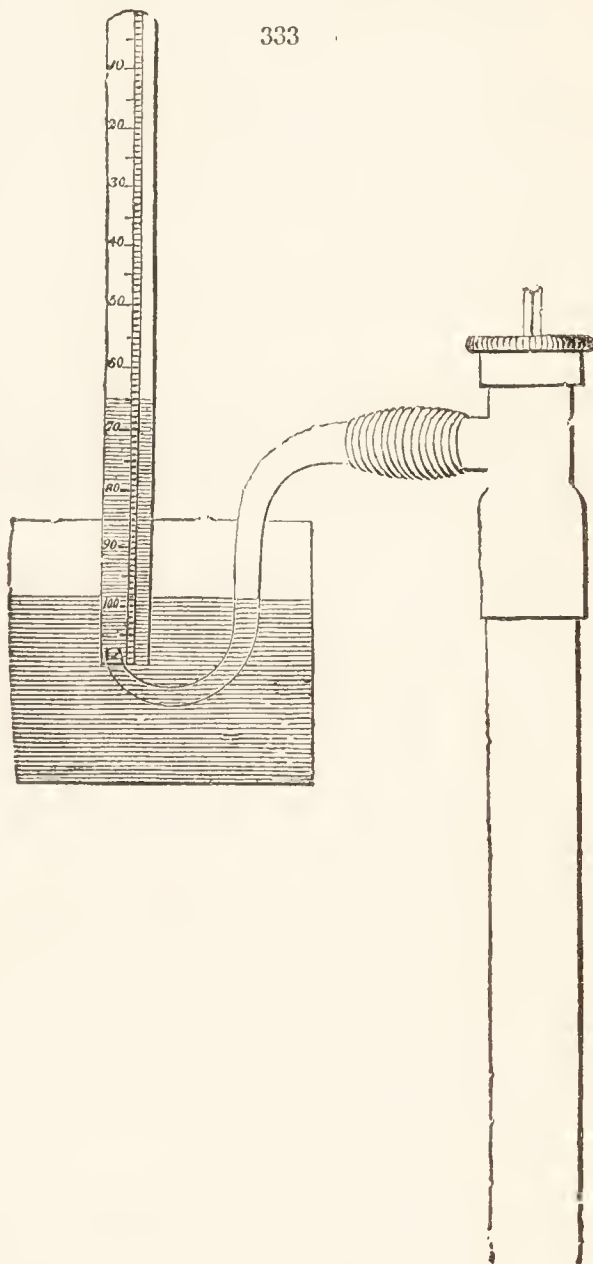
oxygen gas is to be transferred from one siphon to another, through the red-hot tube, with any velocity that may be required, and which may be regulated by means of one of the stop-cocks of the funnels, *RR*, and the stop-cock, *s*, of the opposite siphon.

Such is a general view of the apparatus, and the principles of its operation; but perhaps a few practical remarks on some of the circumstances to be attended to during its employment, may not be deemed superfluous.

\* I have tried various modes of connecting the tube so as to ensure its being air-tight. Caoutchouc answers very well; but the best substance are slips of thin mois-

tened hog's bladder, tied on very tightly with fine *dry* twine. The twine is then to be moistened also, and the whole kept in this state till the end of the experiment.

The substance to be analyzed may be placed in a small tray of platinum-foil, and introduced alone into the tube P, and gradually submitted to the action of heat and oxygen gas; but this does not answer well with organic compounds, as a portion of them is apt to escape combustion. Another method is, to mix the substance with pure siliceous sand, and to retain the mixture in the centre of the tube by means of asbestos. But this method often fails, except there be about an inch of oxide of copper at each end of the tube, which must be kept red-hot during the experiment, and in this case it succeeds completely with many substances. Another method, and that which the most generally succeeds, is to mix the substance with oxide of copper, to heat these together in the tube, in the first place, and afterwards to open the other stop-cock and send the oxygen gas through the ignited and partially reduced oxide, by means of which it again becomes peroxidized; and any portion of the substance that had escaped complete combustion in the first part of the experiment, is now completely burnt. This last method is also that employed when it is required to determine the quantity of carbonic acid gas yielded by a given quantity of any substance; only in this case, of course, oxygen gas is not required, and the contents of the tube P must be taken out and well triturated, and subjected to heat a second time. If it should be required to analyze the gas formed, one method of removing it from the tube, I, is represented at fig. 333; and others will readily occur to the practical chemist.



The following are stated by Dr. Prout to be the advantages of this apparatus and mode of analysis. In the first place, *there is nothing to be apprehended from moisture*. Whether the substance to be analyzed be naturally a hydrate, or in whatever state it may be with respect to water, the results will not be affected; and the great problem, whether the hydrogen and oxygen exist in the substance in the proportions in which they form water, or whether the hydrogen or oxygen predominates, will be equally satisfactorily solved, and that (of course within certain limits), independently of the weight of the substance operated on\*. When, however, it is the object to ascertain the quantities of carbonic

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\* It is to be observed that, throughout the experiments, great care is taken that the gases are *saturated with moisture*; the errors from this cause are thus rendered definite, and are easily corrected by tables calculated for the purpose.

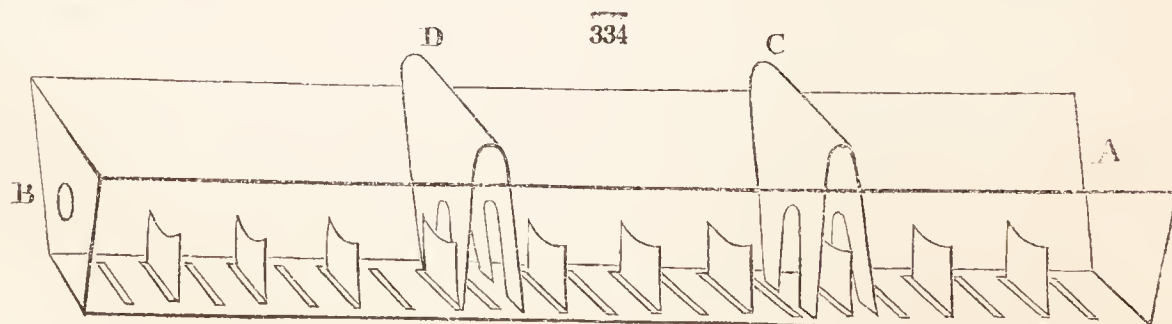


acid gas and water yielded by a substance, it is, of course, necessary to operate on a known weight; but this being once determined, there is no fear, as in the common methods, of exposing the substance to the atmosphere as long as may be necessary. The hygrometric properties of the oxide of copper, as well as its property of condensing air, are also completely neutralized, for the whole, at the end of the experiment, being left precisely in the same state as it was at the commencement, the same condensation of course must take place, and any little differences that may exist are rendered quite unimportant from the bulk of oxygen gas operated on, which of course should, in all instances, be considerably greater than that of the carbonic acid gas formed. Another advantage of this method is, that perfect combustion is ensured by it. There is also no trouble of collecting or estimating the quantity of water, a part of the common process attended with much trouble, and liable to innumerable accidental errors, besides those already mentioned, and which there is no method of obviating or appreciating; here, on the contrary, the results are obtained in an obvious and permanent form, and from the ease with which they are thus verified, comparatively very little subject to error.

The form and principles of this apparatus render it well adapted for many other chemical operations besides the analysis of organized substances. Such, for example, as the reduction of oxides by hydrogen, and a variety of others that will readily occur to the practical chemist.

The preceding details will sufficiently explain the *theory* of organic analysis, but the manipulations and apparatus have of late been much improved by Liebig, Dumas, and others, and the process as now usually carried on, consists in heating the subject of analysis in a glass tube with oxide of copper, in such a way as to burn the carbon into carbonic acid, and the hydrogen into water, the oxygen being estimated by the loss of weight, and the nitrogen either separately collected, or obtained in the form of ammonia.

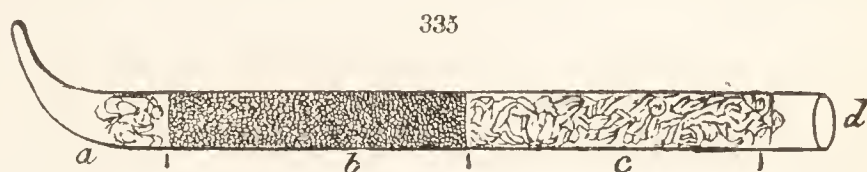
The tubes used in these analyses should be of green glass free from lead, or of the hard Bohemian glass, and generally about four-tenths of an inch in diameter, and from 15 to 18 inches in length, sealed, and either drawn into a point, or rounded at the sealed end: the open extremity should be smoothed by fusion so as to receive a cork without danger of cracking; and it is sometimes proper to protect the tube, by rolling a strip of copper-foil spirally round it, tied at each end by a piece of wire. It may be heated either by means of Cooper's lamp-furnace, (*Quart. Journ.*, xvii. 22,) or over charcoal, in a temporary arrangement of a grate and fire-bricks, (*FARADAY'S Manipul.*,) or in a trough of sheet-iron constructed as follows:—



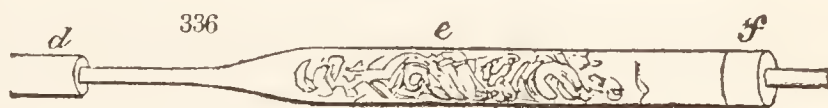
It is about 24 inches long, 3 inches high, 3 inches wide at bottom, and  $3\frac{1}{2}$  at top: the end A is open, and B closed by a perforated plate: there are

slits at the bottom for the admission of air, and a series of supports for the combustion tube; there are also two moveable screens for the purpose of confining the fire to particular portions of the tube. This trough or furnace is placed upon a brick or stone, with its open end very slightly elevated.

When the substance to be analyzed is solid, from 3 or 4 to 8 or 10 grains of it properly dried in the apparatus described at page 310, are carefully mixed with about 200 grains of the dried oxide of copper\*, and introduced into the analysing-tube, into the end of which is previously placed about half an inch in length of small copper-shavings superficially oxidized: these shavings should also occupy about two inches of the tube *above*, or, as it lies horizontally, *before* the organic mixture, the object being to keep the whole contents of the tube in a loose or porous condition, so that the gaseous products may escape from it without impediment. Perhaps the annexed sketch may render



this arrangement more intelligible, in which *a* represents the sealed end containing oxidized copper-turnings, or fragments of the oxide; *b*, the intimate mixture of the oxide with the organic substance, and *c*, the remaining portion of the tube containing copper turnings, or scales of oxide. In this case, the portion *c* is first heated to redness, and the heat is then gradually extended through *b* towards *a*, in such a manner, that all the products may have to traverse the heated oxide; for perfect and entire destruction of the matter subjected to experiment is the essential part of the process. Let us now suppose that the organic substance under examination is a ternary compound of hydrogen, carbon, and oxygen; it is obvious that the products will be *water* and *carbonic acid*: to ascertain the weight of the former, and thence the weight of the *hydrogen* required to form it, the products, as they escape from *d*, may be carried through a tube containing fragments of fused chloride of calcium, and accurately weighed; by this, the vapor of water will be absorbed, and the increase in the *weight* of the tube and its contents, will indicate its quantity: every 9 grains of increase are equivalent to 1 grain of hydrogen. In the following cut (fig. 336), *d* represents the end of the decomposing tube (fig. 335), to which is annexed the chloride of calcium tube *e*, from which issues the smaller tube *f*; the junction at *d* is made air-tight by perforated cork.



The weight of the produced carbonic acid may be learned in two ways; either by collecting it in its gaseous state, and determining its bulk, and

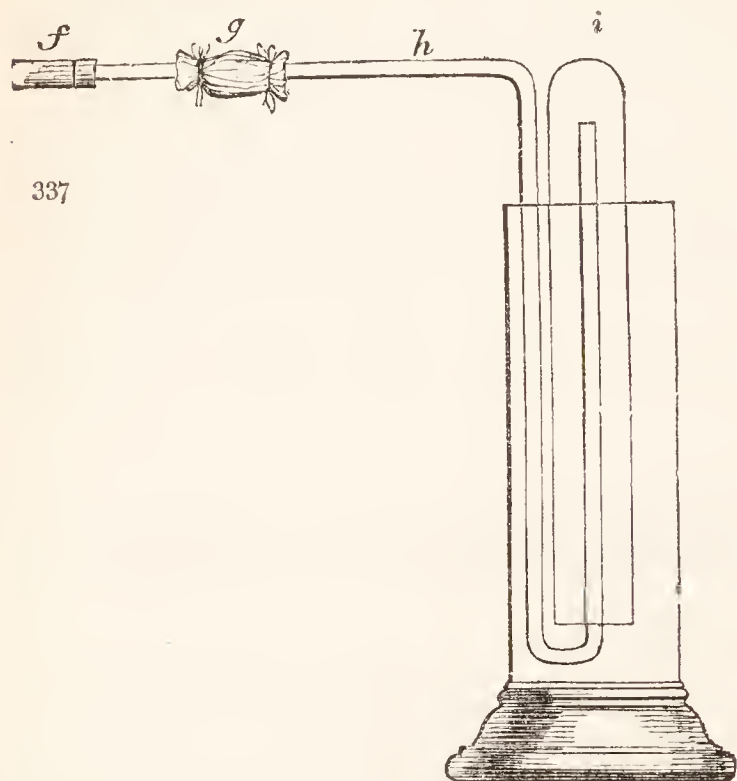
\* According to Dumas, the entire combustion of the whole of the carbon of an organic substance cannot be relied on where oxide of copper only is employed; he therefore introduces into the closed end of the tube about two inches of a mixture of 1 part of chlorate of potassa with 8 of oxide of copper, and as this is last heated, the evolved oxygen passes through the whole extent of the tube, and ensures the conver-

sion of the whole of the carbon into carbonic acid.

*Chromate of lead* has been substituted for oxide of copper as a means of burning organic bodies, and it has the advantage of not being hygrometric. Persoz suggests the employment of sulphate of mercury as a substitute for the oxide of copper. (*Ann. Ch. et Ph.*, LXXV. 6.)



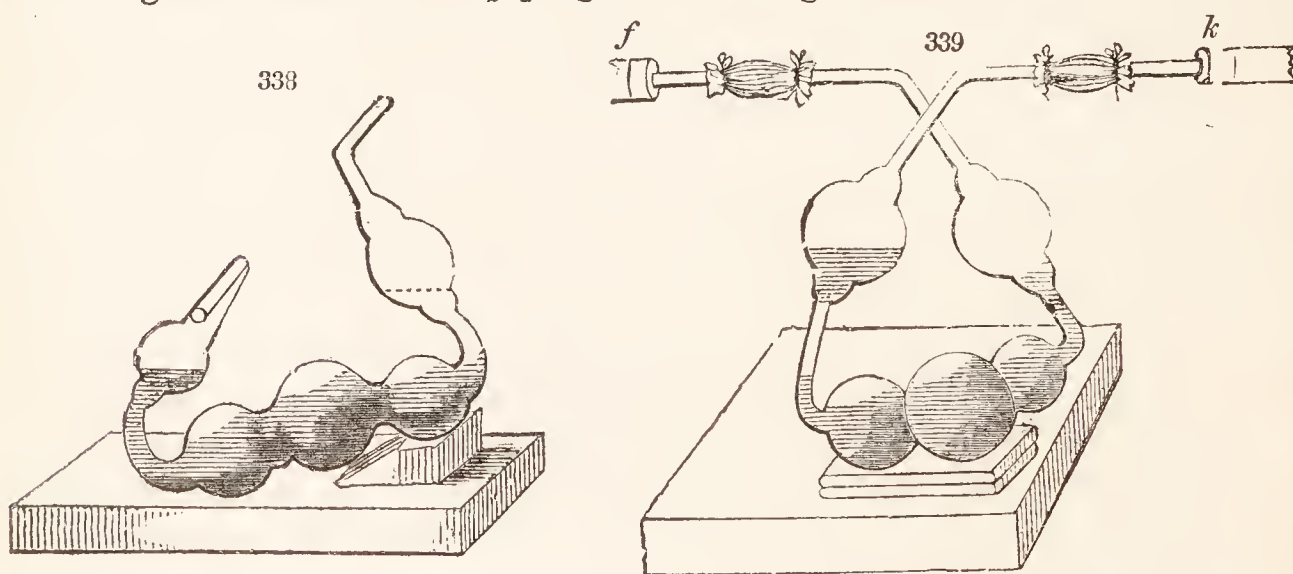
thence deducing its weight and that of the carbon which it contains; or by condensing it into a weighed solution of caustic potassa, and determining its quantity directly by the increase of weight sustained by the solution.



In the former case, the tube at *f* (fig. 337), is connected by the caoutchouc joint *g*, with the bent-tube *h*, the extremity of which terminates in the inverted graduated jar *i*, filled with mercury.

In the latter case, the carbonic acid gas may be conducted from the extremity of the chloride of calcium tube *f*, into the apparatus represented in the annexed cut (fig. 338), which is a glass tube blown into five bulbular enlargements, and containing a solution of caustic potassa. In fig. 339, this

condenser is shown connected with the chloride of calcium tube *f*, by short lengths of caoutchouc piping, and having another tube *k*, containing



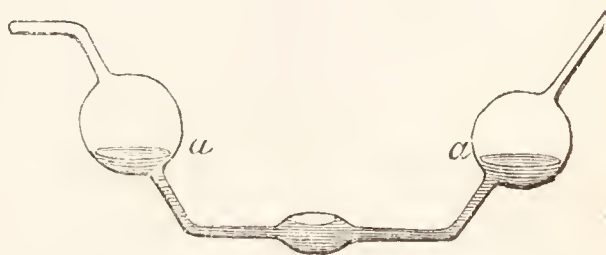
fragments of fused potassa, attached in the same way to its other extremity. This latter tube is only required where *nitrogen* is to be collected, and even then, as I shall presently state, may be dispensed with.

It will be obvious, that after the abstraction of the *water*, in the chloride of calcium tube, the carbonic acid will pass on into the solution of caustic potassa, through which, by properly inclining the apparatus, it may be made to pass in divided bubbles, and under some pressure, so as to ensure its total absorption. When the experiment is completed, the apparatus is allowed to cool, and in order to prevent any portion of the alkaline solution retrograding into the chloride tube, the tip of the analysing-tube near *a* (fig. 335) is broken off, and any residuary carbonic acid may then be drawn into the alkaline solution, by applying gentle suction at the end of the tube *k* (fig. 339). The *weight* of the evolved carbonic acid is determined by accurately weighing the condenser with its alkaline solution, before and after the experiment.

When *nitrogen* is a component of the organic matter under examination\*, the mixture with oxide of copper is made as usual, but the contents of the fore-part of the analysing-tube *c* (fig. 335), must now consist of a mixture of shavings or filings of metallic copper with the oxide, and great care must be taken slowly to conduct the evolved gases through this mixture, rather highly heated, in order to effect the complete evolution of the nitrogen, and to decompose the various compounds which that substance might possibly form with the oxygen, carbon, or hydrogen. The nitrogen then escapes through the tube *k*, (containing fragments of caustic potassa, or of chloride of calcium, to deprive it of humidity,) and must be collected over mercury by connecting the end of that tube with the apparatus *g, h, i*, (fig. 337.) It is, however, in general, better, in cases where the analysis is complicated by the presence of nitrogen, to make a separate experiment for the determination of its quantity: in that case, the evolved gases (carbonic acid and nitrogen,) may be collected in the mercurial apparatus, and the carbonic acid abstracted by a few fragments of fused hydrate of potassa, when the nitrogen will remain, and its weight may then be inferred from the accurate determination of its bulk.

But the most accurate results in respect to the quantitative determination of nitrogen are obtained by converting it into *ammonia*, and in that form combining it with chloride of platinum, so as to weigh it in the state of ammonio-chloride of platinum. (VARRENTRAPP and WILL, *Ann. der Chem. und Pharm.*, xxxix. 257.) For this purpose the azotised organic product, to the amount of 4 or 5 grains, is thoroughly blended in a warm mortar with a mixture of 1 part of hydrate of soda and 2 of lime, in such quantity as to fill the combustion-tube to within about 3 inches of its open end. Attached to the combustion-tube is the annexed three-bulbed apparatus, which is filled up to *a* with pure hydrochloric acid, sp. gr. 1.130. Fire is then applied to the combustion-tube, beginning at the anterior extremity; and when the whole length has been properly heated, air is sucked through it as in the case where oxide of copper is used, and the contents of the bulb apparatus poured into a basin, the bulbs being afterwards washed first with a mixture of alcohol and ether, and then with water, from an ounce to an ounce and a half of liquid being used for that purpose: to the mixture of the hydrochloric solutions and washings, a solution of pure chloride of platinum is added in excess, and the whole

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\* Where mere traces of nitrogen are to be detected, Lassaigne recommends the following process, based on the facility with which cyanide of potassium is formed when azotised organic matter is heated out of the contact of air, with potassium. A piece of potassium, about the size of a millet-seed, is put into a small glass tube, and the substance to be tested upon it; it is then heated to dull redness, and when cold the potassa salt washed out with a few drops of

water, and the solution tested by a drop of sulphate of iron; the dingy precipitate which this forms when brought into contact of a drop of hydrochloric acid, becomes blue if nitrogen were present; if not, it is merely dissolved without any blue tint. Neither caustic potassa nor the carbonate can be substituted for potassium, nor is the method applicable when a nitrate, or an ammoniacal salt are present. (*Bibliothèque Univ.*, April, 1843.)

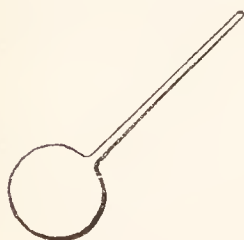


evaporated to dryness: the residue is treated with a mixture of 2 volumes of alcohol, and 1 of ether: if this affords a yellow solution, excess of chloride of platinum has been added, and the remaining washed ammonio-chloride of platinum may be collected on a filter, dried, and weighed: to control the weighing the ammonio-chloride is calcined, and the resulting metallic platinum also weighed: "1.77 parts of nitrogen are indicated by 2.788 parts of the ammonio-chloride, and by 1.233 of metallic platinum." (PARNELL'S *Chemical Analysis*.) According to our equivalents, 14 of nitrogen are indicated by 225 of the ammonio-chloride, or by 99 of platinum: the equivalents adopted by Parnell would give 14 of nitrogen for 220.5 of the ammonio-chloride. All substances containing nitrogen evolve it in this operation in the form of ammonia, except where it is in the state of nitric acid. The objections to this method of determining the nitrogen urged by Reiset (*Ann. Ch. et Ph.*, 3 Ser. v. 469,) have been overruled by Will. (*Proc. Ch. Soc.*, March, 1843.)

When organic bodies contain *sulphur* and *phosphorus*, those substances may be acidified by the action of nitric acid, and their quantities, determined by precipitation by baryta or by oxide of lead; the means of effecting this, and of separating the sulphuric and phosphoric salts have been elsewhere stated.

In the analysis of an organic substance which is extremely volatile, it must, if solid, be fused and weighed in a small glass-tube sealed at one end: this small tube with its contents is then introduced into the combustion-tube, being placed about an inch and a half from the closed end of the latter. If the subject of analysis is a volatile liquid, it is enclosed

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in a small bulb, with a narrow stem (fig. 341), which is weighed before and after the liquid has been introduced. To fill it, it is heated so as to expel part of the air, and whilst hot, its open end is immersed into the liquid, and in this way, by the careful application of heat, the bulb may be nearly filled: its point is then sealed by fusion, and the weight of the included liquid accurately ascertained. In these cases a longer combustion-tube

than usual is requisite, and as the oxide of copper cannot be introduced in a warm state, it must be previously heated and cooled in a close vessel, so as to insure the absence of hygrometric moisture. When cold, a little of it is put into the combustion-tube, and the bulb of liquid is then introduced, its sealed end having been previously broken off; lastly, the tube is filled up with the oxide, and the apparatus arranged as usual. Before the heat is suffered to extend to the bulb so as to vaporise its contents, 6 or 7 inches of the oxide in the fore part of the tube should be red-hot, and the heat afterwards carefully applied so as *very slowly* to vaporise the liquid in the bulb\*.

\* I here insert an outline of the method of determining the specific gravity of *vapors*, which I omitted in its proper place; it is in many cases an operation of much importance, in reference to their atomic constitution: for the minute details of the process, I must refer to Dumas. (*Chim. app. aux Arts*, v. 43.)

A thin glass globe (A, fig. 342) of about

three inches diameter, is drawn out at its neck to a narrow tube six or seven inches long; the point of the tube is cut across with a file and fused but not sealed: it is then weighed, and the temperature and pressure at the time are observed. To introduce the volatile liquid, the globe is warmed so as to expel a portion of its air, and the end of the beak dipped into the liquid. As

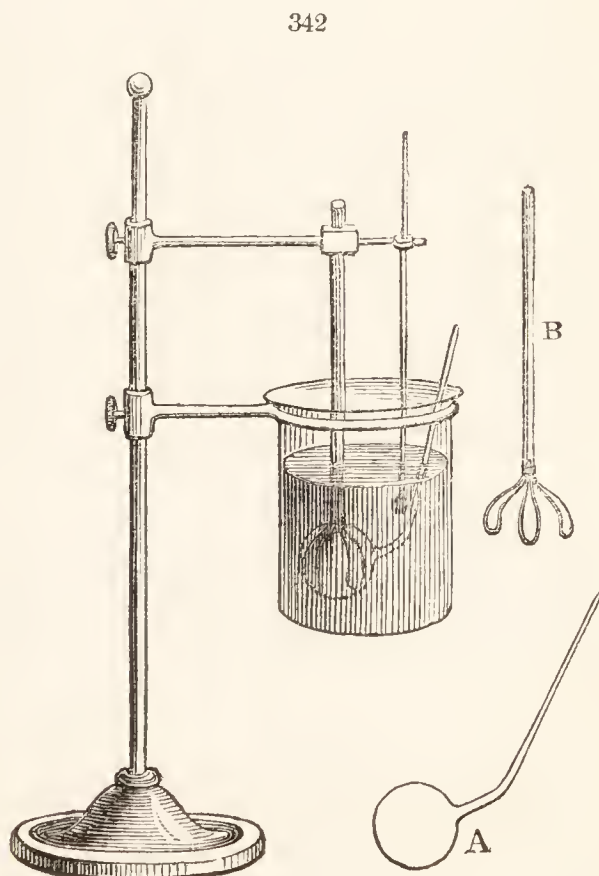
My object in the preceding details, has been to render the *principles* of the ultimate analysis of organic products intelligible to the student; the manipulations, in all their details, scarcely admit of useful description, and can only be learned by practice; and the beginner will do well to make each element the object of a separate experiment; that is, to employ one portion of the matter under examination for the determination of the quantity of water formed, or of the elementary hydrogen; another for the determination of the quantity of carbonic acid formed, or of the elementary carbon; and another for the nitrogen. The most experienced and dextrous chemist will also require repetitions of his analyses; and in undertaking these, he should follow the recommendation of Dumas, who advises that these experiments should be made upon each substance in increasing quantities; one, for instance, upon *two*, one upon *four*, and one upon *six* grains; or in some such proportions.

In the course of the following pages, many instances will occur of the different modes of expressing the ultimate composition of organic bodies, depending, as the following examples will show, upon the parti-

the globe cools, the air within contracts, and the liquid is forced up. When a sufficient quantity has entered (from 100 to 150 grains), the globe is enclosed in the wire holder, and immersed in a bath of water, oil, or other liquid, heated to  $50^{\circ}$  or  $60^{\circ}$  above the boiling-point of the substance in the globe. Under these circumstances a stream of vapor rushes through the orifice, carrying with it the air of the globe. When this ceases, the point of the tube is sealed by a blowpipe flame, the temperature of the bath being observed at the same moment, and the globe is removed from the bath, and when cool is cleaned, and weighed.

The next point to be determined is the capacity of the globe. For this purpose the neck is broken under the surface of water or mercury, when the fluid enters the globe and fills it completely if the operation has been properly conducted. By pouring out the mercury into a jar, graduated to cubic inches, the capacity of the globe is ascertained. We thus obtain the data necessary for the calculation, namely, 1. The weight of the globe full of air at common temperature and pressure; 2. The weight of the globe and vapor filling it at the temperature of the bath and under the same pressure; and, 3. The capacity of the globe.

Having these results, we obtain by calculation, 1. The weight of the empty globe: (by knowing the capacity of the globe the weight of the air contained in it may be calculated, which, deducted from the weight of the globe and air, leaves the weight of the globe when exhausted); 2. The weight of vapor filling the globe at the temperature of the bath (by deducting the



weight of the empty globe from the weight of the globe and vapor); and, 3. The weight of air filling the globe at the temperature of the bath, and at the pressure at which the globe was sealed with the vapor. This last calculation is made according to rules given at p. 365; having performed which, the density of the vapor required is obtained by simple proportion, —As the weight of air filling the globe at the temperature of the bath, is to the weight of vapor filling the globe at the same temperature, so is 1, to the density required, &c.



cular view which may be taken of the secondary combinations of the elementary principles.

It is customary with some chemists to represent the oxygen and hydrogen in certain vegetable substances, by the term *water*, and hence, where these elements are in the ratio to each other of 8 to 1 by weight, and in union with carbon only, the expression *hydrate of carbon* has been applied to the compound. In the following table, which contains the results of the ultimate analyses of several organic compounds, by Gay Lussac and Thenard, the meaning of this expression will be evident, and also of the terms, *excess of hydrogen*, and *excess of oxygen*, as applied to such ternary compounds, in which, as will be observed, nitrogen is not present.

| SUBSTANCES ANALYZED. | Carbon. | Oxygen. | Hydrogen. | Or supposing the Oxygen and Hydrogen to be in the state of <i>Water</i> . |        |                     |
|----------------------|---------|---------|-----------|---|--------|---------------------|
|                      |         |         |           | Carbon.   | Water. | Oxygen in excess    |
| Sugar .....          | 42·47   | 50·63   | 6·90      | 42·47   | 57·53  | 0                   |
| Gum Arabic.....      | 42·23   | 50·84   | 6·93      | 42·23   | 57·77  | 0                   |
| Starch .....         | 43·55   | 49·68   | 6·77      | 43·55   | 56·44  | 0                   |
| Sugar of milk .....  | 38·825  | 53·834  | 7·341     | 38·825  | 61·175 | 0                   |
| Lignin of oak .....  | 52·53   | 41·78   | 5·69      | 52·52   | 47·47  | 0                   |
| „ beech ....         | 51·45   | 42·73   | 5·82      | 51·45   | 48·55  | 0                   |
| Mucic acid .....     | 33·69   | 62·67   | 3·62      | 36·69   | 30·16  | 36·15               |
| Oxalic acid .....    | 26·57   | 70·69   | 2·74      | 33·57   | 22·87  | 50·56               |
| Tartaric acid .....  | 24·05   | 68·32   | 6·63      | 24·05   | 55·24  | 20·71               |
| Citric acid .....    | 33·81   | 59·86   | 6·33      | 33·81   | 52·75  | 13·44               |
| Acetic acid .....    | 50·22   | 44·15   | 5·63      | 50·22   | 46·91  | 2·87                |
|                      |         |         |           |   |        | Hydrogen in excess. |
| Resin (of turpent.)  | 75·94   | 13·34   | 10·72     | 75·94   | 15·16  | 8·90                |
| Copal .....          | 76·81   | 10·61   | 12·58     | 76·81   | 12·05  | 11·14               |
| Wax.....             | 81·79   | 5·54    | 12·67     | 81·79   | 6·30   | 11·91               |
| Olive oil .....      | 77·21   | 9·43    | 13·36     | 77·21   | 10·71  | 12·08               |

They consider it demonstrated, in reference to these experiments, 1st. That a vegetable substance is *acid*, when the oxygen which it contains is, to the hydrogen, in a proportion greater than is necessary to form water; or where there is *excess of oxygen*. 2nd. That a vegetable substance is *resinous*, *oily*, or *alcoholic*, where the oxygen is to the hydrogen in a less proportion than in water, or where there is *excess of hydrogen*; and, 3rd. That a vegetable substance is neither acid nor resinous, but *saccharine*, *mucilaginous*, &c., where the oxygen and hydrogen are in the same relative proportion as in water, or where there is *no excess of either*.

To the correctness of these results, there are, however, exceptions, some of which have been pointed out by Saussure (THOMSON'S *Annals*, vol. vi.), and by Daniell (*Journal of Science and Arts*, vi. 326); but we shall have again to refer to other analyses of the above important pro-

ducts. Certain organic principles, also, which include nitrogen, are not contained in the above table, so that, admitting the general *principle of classification*, it may be modified as follows, in reference to organic proximate principles:—

1. Compounds of carbon, hydrogen, and oxygen, in which the hydrogen and oxygen bear to each other the same relative proportion as in water, and which therefore are represented by  $C + HO$ .

2. Compounds, in which there is excess of hydrogen; represented by  $C + HO + H$ .

3. Compounds, in which there is excess of oxygen; represented by  $C + HO + O$ .

4. Compounds of the above elements, with the addition of nitrogen, represented by  $C, H, O, N$ .

5. There are also some important organic products belonging to the class of *hydrocarbons*, some of which, together with their general distinctive characters, have been already adverted to in the section on Carbon. Although, therefore, it will be necessary often to digress from the arrangement of the vegetable proximate principles suggested by the above considerations, it may be occasionally resorted to as furnishing a general standard of reference.

But the mere determination of the relative proportions of the ultimate elements of these proximate principles, is not the only object of organic analysis; it also views them in reference to the Atomic Theory, in such a way, as to ascertain what number of *elementary atoms* are probably contained in what may be termed the *proximate atom*. The analysis of *morphia*, for instance, shows it to be a compound of 71·91 *per cent.* of carbon, 6·85 of hydrogen, 16·44 of oxygen, and 4·80 of nitrogen: now it is found that 40 parts of sulphuric acid (or 1 equivalent) require 292 parts of morphia for saturation, and assuming sulphate of morphia to be a neutral salt, we should represent the atomic weight of morphia as =292, and we find that this number may, in reference to the proportions of the elements *per cent.*, be assumed as made up of 35 atoms of carbon, 20 of hydrogen, 6 of oxygen, and 1 of nitrogen, as shown in the following tabular statement:

|               | Atoms. |      | Equivalents. |      | Per cent. |
|---------------|--------|------|--------------|------|-----------|
| Carbon .....  | 35     | .... | 210          | .... | 71·91     |
| Hydrogen..... | 20     | .... | 20           | .... | 6·85      |
| Oxygen .....  | 6      | .... | 48           | .... | 16·44     |
| Nitrogen .... | 1      | .... | 14           | .... | 4·80      |
| <hr/>         |        |      |              |      |           |
| Morphia ..... | 1      |      | 292          |      | 100·00    |

Hence the formula of morphia,  $C_{35} H_{20} O_6 N$ . Again, in regard to *sugar*: that substance, in its *anhydrous state*, yields on analysis 47·06 *per cent.* of carbon, 5·88 of hydrogen, and 47·06 of oxygen: now if we divide each of these quantities by the equivalent of their respective elements, the quotients will represent the relations which they bear to each other in equivalents: thus  $47·06 \div 6 = 7·84$ ;  $5·88 \div 1 = 5·88$ , and  $47·06 \div 8 = 5·88$ ; hence sugar would consist of 784 equivalents or atoms of carbon, 588 of hydrogen, and 588 of oxygen: now 784 is to 588 nearly as 12 to 9, so that the formula of anhydrous sugar thus deduced,



would be  $C_{12}H_9O_9$ . If from such a formula, we calculate back to the *per centage*, we shall find how far our estimate is correct:

|       |                        |                      |
|-------|------------------------|----------------------|
| Thus, | 12 atoms of carbon are | $(12 \times 6) = 72$ |
|       | 9 „ hydrogen           | $(9 \times 1) = 9$   |
|       | 9 „ oxygen             | $(9 \times 8) = 72$  |
|       |                        | <hr/>                |
|       |                        | 153                  |

And,

|     |   |    |    |     |   |        |
|-----|---|----|----|-----|---|--------|
| 153 | : | 72 | :: | 100 | : | 47.06  |
| 153 | : | 9  | :: | 100 | : | 5.88   |
| 153 | : | 72 | :: | 100 | : | 47.06  |
|     |   |    |    |     |   | <hr/>  |
|     |   |    |    |     |   | 100.00 |

How far these calculated results agree with those of experiment, will be abundantly evident from the numerous examples which have been elsewhere given.

But there is another important consideration, arising out of these views of the ultimate composition of organic proximate principles, which relates to the different views which may be taken of the manner in which the ultimate elements are arranged, or of the state in which they exist in the original substance, before its decomposition. These views materially affect the perspicuity of our arrangements, as the following instance will serve to show. Ether and alcohol are compounds of carbon, hydrogen, and oxygen; ether is constituted, *per cent.*, of 64.864 carbon, 13.514 hydrogen, 21.622 oxygen. Alcohol consists of 52.174 carbon, 13.044 hydrogen, 34.782 oxygen; now the relative bearings of these numbers are such, as admit of the empirical formulæ of ether and of alcohol being represented by  $C_4H_5O$  and  $C_2H_3O$ : but we also find that the carbon and hydrogen, and the oxygen and hydrogen, are to each other in such proportions as to admit of our considering *ether* as a compound of 2 atoms of *bihydrocarbon* (or olefiant gas), and 1 atom of *water*; and *alcohol* as a compound of 1 atom of *bihydrocarbon*, and 1 of *water*; hence we arrive at certain *rational formulæ*, and instead of the empirical formulæ  $C_4H_5O$ , and  $C_2H_3O$ , we represent ether by  $2[C_2H_2] + HO$ , and alcohol by  $C_2H_2 + HO$ . But we may also regard ether and alcohol as hydrates of *quadrihydrocarbon*, in which case the formula of ether will be  $[C_4H_4] + HO$ , and of alcohol  $[C_4H_4] + 2HO$ . A third view of the constitution of ether and alcohol originally propounded by Berzelius, and for reasons which will afterwards appear, now generally adopted, is founded upon the supposed existence of a hydrocarbon distinct from the former, and having the formula  $C_4H_5$ ; it has been termed *Ethule*, and is regarded as a compound radical of which ether is the oxide, and alcohol the hydrated oxide: thus the formula of ether becomes  $C_4H_5 + O$ , and of alcohol  $C_4H_5O + HO$ .

I might go on to show other theoretic views which may be taken of the atomic constitution of ether and alcohol, and also to apply the same mode of reasoning to the probable proximate arrangements of the ultimate elements in a variety of other organic compounds; I have selected the above as sufficient to point the student's attention to the importance of the subject, and as instances to which I shall afterwards have occasion to refer: the present state of organic chemistry admits of many such

generalizations; such as may be safely adopted, I shall afterwards detail; many are too hypothetical to come within our limits; but the whole subject is of extreme interest, as promising to simplify the apparent confusion and complexity that prevail in reference to the relative proportions of the ultimate elements of organic products, and to enable us to group, or combine them under secondary forms, in many instances analogous to the binary arrangements of inorganic nature, and to apply to them an equally perspicuous nomenclature.

It will now be obvious, that by the adoption of *rational formulæ*, as in the preceding cases of ether and of alcohol, we acquire considerable facility in discussing their combinations and mutual conversions, and that the terms *hydrate* and *binhydrate* of *quadrihydrocarbon*, or *oxide of ethule* and *hydrate of oxide of ethule*, imply much more than the mere *percentage* statements of the elements. We may take a parallel case from the compounds of carbonic acid and ammonia; suppose a compound the ultimate elements of which are stated to be, *per cent.*, 15·35 carbon, 41·05 oxygen, 7·75 hydrogen, 35·85 nitrogen; this statement will be found compatible with, 1 atom of carbon, 2 of oxygen, 3 of hydrogen, and 1 of nitrogen, and such accordingly will be its empirical formula; but we may also so group these elements into two *rational formulæ*, as to represent either *carbonate of ammonia*, or *hydrated carbamide*, as follows:

| Empyric.   |           |        |       | Rational.                                      |                |            |        |
|--|-----------|--------|-------|--|----------------|------------|--------|
| Carbon   | ....1.... | 6....  | 15·38 | Carbonic acid                                  | 1....          | 22....     | 56·40  |
| Oxygen   | ....2.... | 16.... | 41·02 |  |                |            |        |
| Hydrogen   | 3....     | 3....  | 7·70  |  |                |            |        |
| Nitrogen   | 1....     | 14.... | 35·90 |  |                |            |        |
|  |           |        |       | Ammonia  | ....1....      | 17....     | 43·60  |
|  |           |        |       |  | Carbonic oxide | 1....      | 14.... |
|  |           |        |       |  | Water          | .....1.... | 9....  |
|  |           |        |       |  | Amidogen       | ....1....  | 16.... |
| C <sub>1</sub> O <sub>2</sub> H <sub>3</sub> N = 39 100·00 |           |        |       | CO <sub>2</sub> NH <sub>3</sub> = 39 100·00    |                |            |        |
|  |           |        |       | CO <sub>2</sub> HO,NH <sub>2</sub> = 39 100·00 |                |            |        |

Having now adverted to the practical details of the ultimate analysis of organic bodies, we may proceed to examine their *proximate elements* or *immediate principles*; to point out the modes of separating them from each other so as to obtain them in their pure and insulated forms, and to examine their properties, transmutations, and uses. But here, a great difficulty presents itself to the systematic writer, in reference to the *arrangement* to be adopted; for although the number of ultimate elements with which we have to deal is comparatively small, their combinations are apparently infinite, and independent of the peculiarities to which I have already directed the reader's attention, the facility with which they pass into each other, and the opposite characters and habitudes of substances sometimes even identical, but very frequently differing but little from each other in the quality and quantity of their components, are circumstances which, in the present state of chemistry, throw insuperable difficulties in the way of any satisfactory scientific arrangement; such arrangements have, however, been attempted, but it unfortunately happens that the nearer they approach to what has been termed scientific precision, the less are they adapted to fulfil the requirements of the student, that is, to help him in attaining and retaining correct general views of the mutual relations of organic compounds, or to serve as the thread that is to guide him in the progress of his study. Under these



circumstances, therefore, and considering myself as the teacher of the uninitiated, I am obliged to reject the theory of "Compound Radicals" as the basis upon which we are here to proceed; it furnishes no line of distinction between organic and inorganic substances, and merges into an untenable hypothesis when applied to many of the organic groups: it is, however, in some cases importantly available, and enables us to assimilate certain complex subjects of organic chemistry with the simple binary arrangements of inorganic combinations, not only assisting the memory by suggesting sound and useful analogies, but often, for the same reason, facilitating the progress of research or discovery. Under these circumstances, therefore, it is not surprising that we find scarcely any writers agreeing in their views of systematic arrangement as applicable to organic products: each, in fact, has found it necessary to pursue that plan which in his own estimation involves the fewest difficulties, and it is upon such grounds that the following has been selected. I shall begin with certain natural groups of compounds, including substances of very frequent occurrence, and which, with few exceptions, are found in every growing vegetable; they are not associated by any community of composition, some being comparatively simple in their elementary arrangements, others bordering on extreme complexity; some containing, and others not containing nitrogen; and with some of them sulphur and phosphorus are essentially associated: they include the principal elements of animal nutrition, and many of them are common to both of the organic kingdoms. The principal organic acids and alkaloids will then be examined; and afterwards the resins and essential oils, and coloring principles; and such information connected with these subjects as could not conveniently be given under the preceding heads, will be found in an alphabetical list of certain plants which have been more or less subjects of chemical examination. The phenomena of fermentation will then be discussed, leading to the history of alcohol and acetic acid, and their derivatives and analogues. The chemistry of the blood, the animal secretions and excretions, and of the functions of organic beings, will conclude this part of the subject.

## § II. STARCH: ITS CONGENERS AND METAPHORPHOSES.

STARCH, or *Fecula*, is a common and even abundant principle in the greater number of vegetables. It is contained in the esculent *grains* and other *seeds*, in many *bulbs*, *rhizomes*, and *roots*, in the *stems* of several species of *palm*, and in different *lichens*; and some *fruits*, such as apples and pears, contain a considerable quantity of it at particular periods of their growth. The usual process for obtaining starch consists in diffusing the powdered or bruised grain or seed, or the rasped root, bulb, or stem, in cold water, which becomes white and turbid; the grosser parts may be separated by a strainer, and the milky liquor which passes deposits the starch, which is then to be well washed in cold water, and dried in a gentle heat.

*Common or Wheat Starch* was formerly obtained by steeping wheat in water till it became soft and swollen, when it was put into coarse linen bags and subjected to pressure in a vat filled with water; the milky juice which exuded became thus blended with the water in the vat, and the starch gradually subsided: the supernatant liquor soon underwent a

slight fermentation, giving rise to the formation of a little alcohol and ultimately of acetic acid, by which some of the impurities of the deposited starch were dissolved; it was then collected, washed, and dried in a moderate heat.

Starch is at present obtained chiefly from wheat, from rice, or from potatoes, and the largest manufacturers are resident in or near London. When wheat is used it is coarsely ground and put into a vat with a sufficient quantity of cold water, in which it lies and ferments, sometimes seven or eight days, and at others longer, according as it may be wanted, or as the weather promotes or retards fermentation. When the fermentation is over, which is known by the starch settling at the bottom of the vat, the whole is taken out by small quantities at a time, and put into hair sieves and washed with water, which separates the bran from it, the fine parts running through the sieve with the water into shallow tubs, or vessels, called *frames*. The fermentation becomes acetous, and what runs through the sieves contains the starch suspended in a very foul acid liquor, called *sour water*. In about two days after this operation, the starch settles at the bottom of the frames, the sour water is then drawn off, and the dirty discolored part, which is the last that subsides, and therefore is at the top, is scraped off; the surface of the remaining starch is then washed, till it is nearly free from the mucilaginous sediment. The top, called *slimes*, is put into another frame or tub, and treated similarly, to obtain the starch from it. The starch is stirred with fresh water and strained through a finer sieve into another frame or tub, when, being nearly cleansed of its impurities, it is called a *green water*. In two or three days the starch settles at the bottom of the frame or tub, where it is kept till it is either washed again or *boxed*. If it is washed again, in the manner above described, the part washed off is called a *white water*, instead of a *slime*; the other part being still called a *green water*. The starch, being sufficiently pure and settled, is taken out of the frames or tubs, and put into oblong boxes, about five feet long and one broad, with holes in the bottom and lined with linen cloth, to drain and harden, where it soon becomes solid enough to be cut into square lumps: it is then turned out of the boxes and laid upon bricks (which absorb the moisture) for two or three days to dry. When sufficiently hard, the pieces are put into the *stove*, a square building fitted up with racks on every side, at proper distances for receiving the pieces, and heated from below. Here they remain in a moderate heat for about two days, till a slimy crust forms on the surface. When taken out of the stove, the crusted part is carefully scraped off, and the remainder, which is now perfect starch, is papered, labelled, and stamped, and placed again in the stove, with a good fire, for about three days, till quite dry. During this drying the lumps crack pretty uniformly into the small pieces in which they appear when sold. The slimes and white waters are treated in the same way, till all the starch is got from them, and boxed, drained, and dried, as before. (See the *Eighth Report of the Commission of Excise Inquiry*, 1834.)

The preparation of a good starch from *rice* long baffled the manufacturer, until Mr. Orlando Jones, in the year 1841, (see the specification of his patent in the *Repertory of Inventions*, April, 1841,) devised the ingenious method of separating it from rice flour by the action of a very



dilute solution of caustic soda (200 grains to the gallon of water), which dissolves the gluten and sets the starch free, which is then washed and dried as usual; so that by this operation the process of fermentation is rendered unnecessary. The principal requisite caution in this case is to employ the caustic alkaline solution of a proper strength; if too weak gluten and other matters escape its action, and if too strong the starch is deteriorated or even dissolved.

To obtain starch from *potatos* they are well washed and reduced to a pulp by a rasping machine; this pulp is then elutriated upon a sieve so as to wash out the starch and leave the fibre or parenchyma; the turbid water is then allowed to settle in a vat or back, and by running off the supernatant liquor into a second and third vessel, starch of different fineness or purity is successively deposited: it is stated that about 17 or 18 *per cent.* of starch is the average produce of good *potatos*. This starch is sometimes sold under the name of *English arrow root*, and an imitation sago is manufactured from it in France. Several other varieties of starch are known in commerce, and are chiefly used as articles of food and diet, such as arrow root, sago, tapioca, tous les mois, &c.

*West Indian Arrow Root* is a very pure form of starch obtained from the tubers of the *Maranta arundinacea*: that from Bermuda is most esteemed. To prepare it for use it should first be well mixed with cold water to the consistency of thin cream, and boiling water should then be added under constant stirring, when it dissolves into an uniform pasty mixture: a small tablespoonful of arrow root will suffice for a large pint basin, to which sugar, wine, and a little nutmeg are usually added. *East India Arrow Root* is the starch of the roots of certain species of *Curcuma*.

*Sago* is obtained from the pith or central tissue of the stems of several kinds of palms, especially those of the genera *Sagus* and *Saguerus*. It is usually met with in buff-colored granules called *pearl sago*, which are sometimes deprived of color by bleaching: it yields a gelatinous solution when carefully stirred into boiling water. Another variety is called *brown sago*; it is granulated from the size of pearl barley to that of a small pea. Sometimes it is imported in the form of a whitish powder called *sago meal*, but for dietetic use, pearl sago is almost exclusively resorted to: it should be free from taste and smell.

*Tapioca* is the starch of the *Janipha Manihot*; it is imported from the Brazils generally in small irregular lumps: when in powder it is sometimes termed *Brazilian arrow root*: it yields a more consistent jelly than most other kinds of starch.

*Canna Starch* or *Tous les Mois* is said to be obtained from the rhizome of the *Canna coccinea*; it is imported from St. Kitts, and is an excellent substitute for arrow root.

*Otaheite Arrow Root* is the starch of the *Tacca pinnatifida*, and *Portland arrow root* is obtained in the Isle of Portland, from the tubers of the *Arum maculatum*.

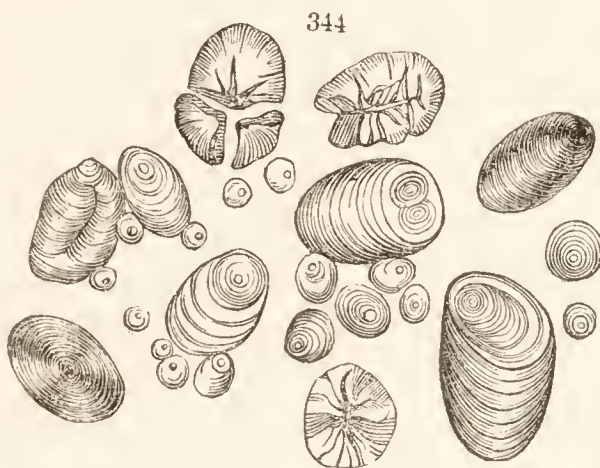
When these varieties of starch are examined by a microscope they are seen to consist of small rounded or spheroidical grains differing in size and somewhat in shape, according to the source whence they are derived. Their size, form, and other peculiarities have been minutely described by Payen, Raspail (*Chimie Organique*), and others. The annexed representations are from Dr. Pereira's *Treatise on Food and Diet*, and are



drawn to one scale ; they often enable us to detect mixture of one kind of starch with another, and to ascertain its presence in cases of adulteration. On some part of the grain a small spot or fissure may be observed, which has been called the *hilum*, and which has sometimes been regarded as the spot where the granules adhered to the cell containing them. The grains represented in fig. 349, with a black cross, show their characteristic appearance when viewed by polarised light.



Wheat Starch.



Potato Starch.



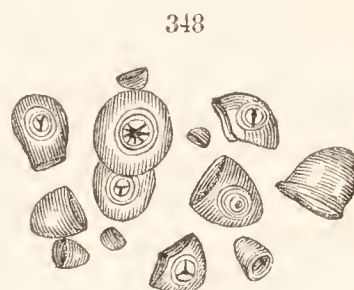
West Indian Arrow Root.



East Indian Arrow Root.



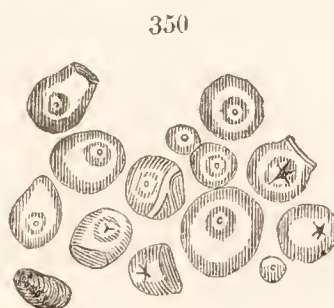
Sago Meal.



Tapioca.



Tous les Mois, or Canna Starch.



Otaheite Arrow Root.



Portland Arrow Root.

Ordinary starch appears as a snow-white and often somewhat glistening powder, which when pressed by the fingers produces a peculiar crackling noise. Its specific gravity is about 1.5. When heated to  $212^{\circ}$ , it loses more or less adherent water, and gradually becomes anhydrous : at a higher temperature (between  $390^{\circ}$  and  $400^{\circ}$ ) it acquires a yellow tint, and, losing the characters of starch, acquires those of gum, a change which will afterwards be more fully noticed. Jacquelin found that on subjecting a viscid solution of starch to a temperature of about  $300^{\circ}$ , for two hours, in a Papin's digester, it yielded a thin liquid admitting of filtration at  $212^{\circ}$ , and depositing a white powder on cooling, which,



examined by a microscope, proved to be composed of very minute granular or spherical particles, scarcely soluble in cold water, but more soluble at 158°, and readily soluble at 212°; they were insoluble in alcohol, and rendered blue by iodine: their ultimate composition agreed precisely with that of the original starch. The mechanical peculiarities of starch in this form are remarkable. (*Ann. Ch. et Ph.*, Lxxiii. 167.)

In its ultimate composition, starch, like gum, may be represented as a *hydrate of carbon*\*; its elements are such as to lead to the formula C<sub>12</sub>H<sub>10</sub>O<sub>10</sub>, or C<sub>24</sub>H<sub>20</sub>O<sub>20</sub>; under the first formula its equivalent will be 162, and it will be represented by C<sub>12</sub>,10HO; or

|                  |    |      |     |      |        | Berzelius. | Gay Lussac<br>and Thenard. | Prout. |        |      |        |
|------------------|----|------|-----|------|--------|------------|----------------------------|--------|--------|------|--------|
| Carbon .....     | 12 | .... | 72  | .... | 44·44  | ....       | 44·250                     | ....   | 43·55  | .... | 42·30  |
| Hydrogen .....   | 10 | .... | 10  | .... | 6·17   | ....       | 6·674                      | ....   | 6·77   | .... | 6·35   |
| Oxygen .....     | 10 | .... | 80  | .... | 49·39  | ....       | 49·076                     | ....   | 49·68  | .... | 50·85  |
| <hr/>            |    |      |     |      |        |            |                            |        |        |      |        |
| Anhydrous starch | 1  |      | 162 |      | 100·00 |            | 100·000                    |        | 100·00 |      | 100·00 |

\* It would appear from Dr. Prout's researches, that there is a slight variation in the proportion of the elementary water of the different starches, as is more distinctly the case in the different sugars: thus, he found the starch of wheat, arrow root, and potatos, carefully dried at 212°, to give the following results:—

| Wheat Starch. |        |      | Arrowroot. |      |        | Potato Starch. |  |  |
|---------------|--------|------|------------|------|--------|----------------|--|--|
| Carbon        | 42·80  | .... | 44·40      | .... | 44·25  |                |  |  |
| Water         | 57·20  | .... | 55·60      | .... | 55·75  |                |  |  |
| <hr/>         |        |      | <hr/>      |      |        | <hr/>          |  |  |
|               | 100·00 |      | 100·00     |      | 100·00 |                |  |  |

He supposes that there are *low* starches as well as *low* sugars; wheat starch he places at the head of the starches, and considers arrow root as the lowest variety. “Whether arrow root,” he observes, “be the lowest that exists, I am unable to say; but I have met with none lower; and have reason to believe that the greater portion of the other varieties of the amylaceous principle known to exist, like the varieties of sugar above given, are intermediate in their composition between arrow root and wheat starch.

“The identity of composition between wheat starch and cane sugar, and between the sugar of honey and arrow root, seems to show that, though these bodies are not actually capable of assuming the crystalline form, yet the original tendency among their essential elements to combine in certain proportions (and perhaps to assume certain forms) still continues to operate, though in a mitigated degree, and thus to exert, as it were, a feeble *nisus*, or endeavour toward the maintenance of certain definite modes of existence.”

In reference to what are usually called the *extraneous* or foreign ingredients of certain vegetable principles, Dr. Prout has the following remarks:—

“It has been known from the very infancy of chemistry, that all organized bodies, besides the elements of which they are essentially composed, contain minute quantities of different foreign bodies, such as the earthy and alkaline salts, iron, &c. These have been usually considered as mere mechanical mixtures accidentally present; but I can by no means subscribe to this opinion. Indeed, much attention to this subject for many years past, has satisfied me that they perform the most important functions; in short, that organization cannot take place without them. This point will be more fully investigated hereafter: at present it is sufficient merely to observe, that many of those remarkable changes which crystallized bodies undergo on becoming organized, are more apparent than real; that is to say, their chemical composition frequently remains essentially the same; and the only point of difference that can be traced, is the presence of a little more or less of water, or the intimate mixture of a minute portion of some foreign fixed body. There is no term at present employed which expresses this condition of bodies, and hence, to avoid circumlocution, I have provisionally adopted the term *merorganized*, (*μέρος, pars vel partim,*) meaning to imply by it that bodies on passing into this state become partly, or to a certain extent, organized. Thus starch I consider as *merorganized* sugar, the two substances having, as we shall see presently, the same essential composition, but the starch differing from the sugar by containing minute portions of other matters, which, we may presume, prevent its constituent particles from arranging themselves in the crystalline form, and thus cause it to assume totally different sensible properties.”

In its ordinary state starch is insoluble in cold water, alcohol, and ether. If boiling water be poured upon it it forms clots which cannot afterwards be uniformly diffused, hence the precaution above adverted to, in first diffusing it through cold water and then gradually stirring it with the heated water, when an uniform gelatinous mixture is required. There is much difference of opinion as to the real nature of what is termed a *solution* of starch, and as to the action of hot water upon the organized spherules. It seems probable that these consist of concentric layers, the exterior of which is less easily acted upon by hot water than the interior; that the first effect of the heated water is to swell and burst the granule; that the interior portions are then to a certain extent dissolved, and that the harder exterior parts resist the action of the water for a longer time, and remain diffused through it, giving it its semi-opacity, and being gradually deposited as a bulky sediment, if the liquor be sufficiently dilute to allow of its subsidence. If the portion which is apparently dissolved be passed through a filter, it is transparent and colorless, and presents all the characters of a true solution of starch: if frozen and then carefully thawed again, it becomes more or less opaque and a flocculent deposit of starch separates: if carefully evaporated to dryness, it leaves a gumlike residue, which, however, warm water again dissolves, and the solution has all the characters of the original. There seems little doubt therefore that in this way water at a certain temperature has the property of dissolving starch; but it is also probable, from the appearances which ensue during its action, and from the metamorphic tendencies of starch, that it may undergo some peculiar changes by the joint action of heat and water, independent of mere solution. The different varieties of starch are more or less easily acted on by hot water, dependant perhaps upon the different dimensions and degrees of induration of their granules, but the general results are as follows: 1 part of starch diffused through 15 parts of cold water, and kept constantly stirred, undergoes no apparent change till heated to about  $130^{\circ}$ , when the smallest globules begin to be acted upon, and some of them bursting, yield what appears to be soluble matter to water; as the temperature increases, the same results ensue with the larger globules, and at about  $175^{\circ}$ , they swell up into a gelatinous mass and begin successively to burst and emit their contents, and this goes on increasing till the liquor approaches or attains its boiling-point, when a perfect gelatinous mixture is formed, which, however, is separable on dilution and subsidence, into a perfectly transparent solution and an opalescent deposit: the portion of the starch grain which has thus been to all appearance perfectly dissolved, and which remains in solution on cooling, and passes the filter, has sometimes been termed *amidine*, in order to distinguish it from the original granular starch. What is usually termed starch jelly, or paste, consists of the swollen globules diffused through the aqueous liquor, each globule apparently occupying in its distended state, from 30 to 40 times its original volume. But although cold water is without apparent action on starch granules in their original and ordinary condition, it appears that they only resist its action in consequence of their indurated exterior; for if the starch be comminuted by trituration, so as to break the granules, and then rubbed up with cold water, the filtered liquor will be found to hold traces of amidine in solution.

One of the most characteristic properties of starch is that of forming



a deep blue compound with iodine; and accordingly this color is produced whenever a solution of iodine is added to a solution of starch, or to starch diffused through water, or when starch and iodine are triturated together: this test, therefore, when properly applied, enables us immediately to detect the presence of starch in any of its forms. The nature of this blue compound has not been satisfactorily ascertained, and it does not appear that its components are united in equivalent proportions, nor does there seem any reason, on the other hand, for supposing that the blue color is merely finely divided iodine "adhering to the starch as a dye does to the fibres of cloth." The tint and characters of the blue compound vary with the circumstances of its formation and composition; it appears to be soluble in pure water but insoluble or very sparingly soluble in acid or saline liquors: its tint is destroyed by heat, so that if the deep-blue liquor obtained by mixing aqueous solution of iodine and starch be poured into boiling water, the color vanishes; but it reappears as the liquor cools, unless it has been continuously boiled, in which case other reactions ensue. When the varieties of dry starch are put into an aqueous solution of iodine, the granules are more or less affected in consequence probably of their varying texture and dimensions; some become deep blue or nearly black; others pale blue; and others at first assume a pink hue; but if the starch and iodine be triturated together an uniform deep blue compound is produced. (The effects of iodine on different kinds of starch have been described by Goble. *Chem. Gaz.*, May, 1844.) The same compound is obtained by adding aqueous chlorine to a mixed solution of starch and iodide of potassium, or by precipitating a clear solution of starch in dilute hydrochloric acid, by an alcoholic solution of iodine. When collected on a filter, washed with a little cold water, and dried over sulphuric acid, it forms an intense blue gumlike substance, which is somewhat deliquescent. The blue solution of the pure iodide may be kept without change, but if it contain hydrochloric or sulphuric acid it gradually loses color. It is bleached by sulphuretted hydrogen in consequence of the formation of hydriodic acid; so that the blue liquor has been used as a quantitative test of the sulphuretted hydrogen present in mineral waters. Chlorine, bromine, sulphurous acid, arsenious acid, corrosive sublimate, the alkalis, and excess of alcohol, also decompose the iodide of starch and abstract its iodine: and its aqueous solution is bleached by the sun's rays in consequence of the formation of hydriodic acid, and the blue color is restored by the careful addition of a little chlorine or nitric acid, which again evolve iodine. The detection of iodine in mineral waters by this test is best effected by evaporating the water to a small bulk, adding to it a little pasty starch, and then carefully dropping in nitric acid, or weak solution of chlorine. If the presence of iodic acid be suspected in a liquid, it may be mixed with the starch and aqueous solution of sulphurous acid gradually added. Electric decomposition may also be made available for the application of this test (p. 222). If characters be written upon white paper with a solution of starch containing a little iodide of potassium, they are invisible when dry, but immediately become blue or purple on the approach of a little chlorine or nitric vapor, forming therefore a *sympathetic ink*.

When an aqueous solution of bromine is added to a hydrochloric solution of starch, a yellow precipitate falls, but it loses bromine when

dried at common temperatures. The peculiar color imparted by starch to sea water concentrated by evaporation and mixed with a little solution of chlorine, led Balard to the discovery of bromine. Starch and chlorine do not apparently form any analogous combination, but when starch is exposed to chlorine a gradual decomposition ensues, attended by the formation of a brown semifluid substance, and hydrochloric and carbonic acids.

Under the influence of certain reagents, and especially of the dilute acids, starch is susceptible of various transmutations which will presently be separately noticed. When mixed with concentrated sulphuric acid it forms a black magma, sulphurous acid is evolved, and on the addition of water, more or less carbon is generally thrown down. If it be carefully triturated with the acid so as to avoid elevation of temperature, it becomes perfectly soluble in water, and is apparently changed into gum (or dextrine), but if in that soluble state carbonate of lime, baryta, or lead, be added, peculiar soluble and crystallisable salts of those bases may be obtained, which have been termed by Blondeau de Carolles *Sulphamido-nates*. (LIEBIG, *Chimie Organique*, iii. 7.)

According to Saussure, a crystallizable compound of starch and sulphuric acid may be obtained by dissolving, in a gentle heat, 1 part of starch in 3 of sulphuric acid, previously diluted with 36 parts of water, and mixing the solution with alcohol, which throws down a precipitate composed of starch and *sulphate of starch*; when washed with alcohol, dissolved in a small portion of water, and left to spontaneous evaporation, acicular crystals of sulphate of starch are formed, from which the free acid, contained in the mother-liquor, may be washed with alcohol. These crystals are not perfectly soluble in water without slight decomposition. (*Ann. Ch. et Ph.*, xi. 385.)

When starch is triturated with fuming nitric acid it forms a transparent jelly, and on the addition of water a white granular precipitate falls, which has been termed by Braconnot, *Xyloidine*; it consists, according to Ballot (*Ann. der Chem. und Pharm.*, Jan. 1843), of two principles separable by a dilute solution of caustic potassa; the undissolved portion is white and pulverulent; the substance dissolved forms a white flocculent precipitate on the addition of acetic acid. *Xyloidine* (or *Nitramidine* of Dumas), when boiled in water, becomes soft and viscid, but does not dissolve: it is soluble in hot hydrochloric acid, and precipitable from the solution by water; with concentrated sulphuric acid it forms a limpid solution, which remains clear on dilution: it is very soluble in cold dilute nitric acid, and, when boiled, this solution yields oxalic acid, but no mucic acid; it is precipitated by the alkalis: concentrated acetic acid readily dissolves *xyloidine* into a thick mucilage, with which water forms a white coagulum; when this acetic solution is evaporated, it leaves a transparent residue, and, if spread on paper or wood it forms a brilliant varnish, which resists the action of water. *Xyloidine* is not soluble either in cold solution of ammonia or of caustic potassa; but in the latter it becomes viscid, and, when heated, gives a brown solution. It is nearly insoluble in alcohol. It is very inflammable. According to Pelouze, *xyloidine* consists of  $C_6H_4O_4$ ;  $NO_5$ . According to Ballot, its components are more correctly represented by  $C_{15}H_{12}O_{16}N$ . Starch dissolves in the greater number of dilute acids, forming thin solutions, which,



when boiled, give rise to the formation of gum and sugar, as will presently be explained.

With caustic potassa and soda, starch, in its ordinary granular condition, furnishes a viscid magma, soluble in water and alcohol, and from which the alkalis throw down a precipitate of somewhat modified starch or amidine: if the alkaline solution is very dilute, the starch globules are not affected, but any gluten which may be present with them is dissolved, as has already been mentioned in reference to the preparation of *Rice starch*. Potato starch is more readily dissolved by the alkalis than wheat starch.

Lime and baryta form with starch insoluble compounds, which fall when a solution of starch is added to lime or baryta water. When a boiling solution of starch is mixed with subacetate or subnitrate of lead, a white curdy compound falls, and the subsalt becomes neutral. The precipitate consists, according to Berzelius, of 72 starch + 28 oxide of lead, being  $= 4\text{PbO} + \text{C}_{24}\text{H}_{20}\text{O}_{20}$ . None of the combinations of starch with the salts are interesting or important. It exerts, however, according to Vauquelin, an evident solvent power over phosphate of lime. According to Rose, the presence of starch prevents the precipitation of oxide of iron by the alkalis.

Starch combines with tannin, and the compound is best obtained by filtering a hot solution of starch in infusion of galls; as it cools, the *tannate of starch* falls. It is thrown down when a strong infusion of galls is mixed with one of starch, but the precipitate dissolves on the application of heat. Starch is not thus precipitated by all the varieties of tannin, nor does it apparently combine with artificial tannin.

**CONGENERS OF STARCH.** *Inulin*. This modification of starch was discovered in 1804, by V. Rose, in the root of the *Inula helenium*; it has been found by Payen (*Ann. Ch. et Ph.*, xxvi. 102), in the tubers of the dahlia, and also in other plants, so that a variety of names have been given to it in reference to its sources, such as *Dahline*, *Menyanthine*, *Datiscin*, &c. Rose obtained it in the form of a white precipitate, deposited during the cooling of a strong decoction of elecampane root. Payen procured it from the grated root of the dahlia, which was first washed with cold water, then boiled with the addition of a little chalk, strained, filtered through charcoal, and clarified by white of egg: it was then evaporated till a pellicle formed upon the surface; during cooling the inulin was deposited to the amount of 10 *per cent.* of the original root. The expressed juice of the potato also yields a little inulin (about 3 *per cent.*) when evaporated.

Inulin is purified by dissolving it in hot water, and cooling the solution, when it is deposited in the form of a white, insipid, inodorous, granular powder, specific gravity 1.356. Heated a little above  $212^{\circ}$ , it loses water and fuses. Iodine renders it yellow. It is insoluble in cold, but sparingly soluble in boiling alcohol: dilute acids dissolve it, and readily convert it, by boiling, into gum and sugar. In other respects, also, it is analogous to common starch. According to Parnell, its formula, when dried at  $212^{\circ}$ , is  $\text{C}_{24}\text{H}_{21}\text{O}_{21}$ . Its ultimate composition has, however, been variously represented. (See *Chem. Gaz.*, May 1, 1846.)

*Lichen Starch.* *Lichenin*. Most lichens contain a species of starch:

it may be obtained from the *Cetraria islandica* as follows: it is cut into shreds, and infused in about 18 parts of cold water, to which carbonate of potassa is added in the proportion of 120 grains to each pound of moss. After 24 hours the moss is drained upon a sieve (not *pressed*), and thoroughlyedulcorated by cold water; it is then boiled in nine pints of water down to six, and the decoction strained and squeezed out whilst hot. The strained liquor, at first clear and colorless, becomes, on cooling, a grey opaque jelly, which, if suspended in a cloth, or dried on blotting-paper, becomes hard as it dries, and of a dark color. Redissolved in boiling water, it may be again gelatinized. It is tasteless, insoluble in alcohol and ether, contains no nitrogen, and yields on destructive distillation the same products as potato starch. It is only slightly soluble in cold water, and when long and repeatedly boiled it loses its property of gelatinizing. Iodine renders it dingy green. The dilute acids prevent its gelatinization, and gradually change it into gum and sugar. It is copiously precipitated by subacetate of lead; but, in many other respects, it resembles common starch. According to Mulder, lichen starch is represented by  $C_{24}H_{20}O_{20}$ .

A variety of other substances have occasionally been ranked with these modifications of starch, but several of them approach nearer to gum or mucilage, under which they are noticed, and others, not adequately examined, will be elsewhere adverted to.

**METAMORPHOSES OF STARCH.** Under this head I shall consider the various circumstances under which starch is susceptible of conversion into certain modifications of gum and sugar.

1. It has already been observed, that when starch is dried at  $212^{\circ}$  it loses more or less weight in consequence of loss of hygrometric moisture, but that at higher temperatures it becomes modified in solubility and properties. When carefully heated till vapor rises from it, it becomes soluble in cold and hot water, and loses its gelatinous character. Instead of blue, iodine gives it a dingy purple tint. Starch, thus altered by heat, is known in commerce under the name of *Torrefied starch*, or *British gum*, and is often used as a substitute for gum arabic, in the processes of calico-printing, and for stiffening different goods. It is commonly sold in Paris under the name of *Dextrine*, a term applied to it in consequence of its characteristic property of turning the plane of polarisation to the *right*, when acting on polarized light: it has also been called *Leiocome*: this latter term is chiefly applied to a modified dextrine, prepared by a method discovered by Payen, and which furnishes a whiter and more soluble product than can be obtained by torrefaction: it consists in moistening 1000 parts of dry starch (potato starch is generally used) with a very dilute nitric acid, consisting of 2 parts of concentrated acid and 300 of water: the mixture is divided into small blocks, which, when dried in the air, are rubbed down, and exposed in a proper drying stove to a current of air heated to about  $150^{\circ}$  or  $160^{\circ}$ : the powder is ultimately well dried, at a temperature not exceeding  $230^{\circ}$ . When well made, it dissolves in cold, or slightly warmed water, with the same facility as gum.

2. When a cold aqueous solution of pure starch is kept, in or out of the contact of air, for six or eight weeks, water being occasionally added to prevent desiccation, and the temperature between  $60^{\circ}$  and  $80^{\circ}$ , a portion



of gum and of sugar is gradually formed in it. (SAUSSURE, *Ann. Ch. et Ph.*, xi. 379.) The following table shows more explicitly the nature of these changes.

|                           | A            | B       | C      | D        | E      | F      |
|---------------------------|--------------|---------|--------|----------|--------|--------|
| Sugar .....               | 37·00        | 47·4    | 49·7   | 35·4     | 30·4   | 1·00   |
| Gum                       | } Dextrine ? | } 10·00 | } 23·0 | } 9·7    | } 17·5 | } 17·2 |
| Amidine                   |              |         |        |          |        |        |
| Starch .....              | 5·83         | 4·0     | 3·8    | 9·4      | 9·3    | 98·00  |
| Ligneous starch .....     | 10·53        | 10·3    | 9·2    | 7·0      | 4·4    |        |
| Carbonaceous lignin ..... | trace        | trace   | 0·3    | trace    | 0·2    |        |
| Soft resin .....          | 0·30         |         |        | loss 6·0 |        |        |
|                           | 77·96        | 93·6    | 77·9   | 94·0     | 78·5   | 100·36 |

A is the composition of the residue of 100 parts of *wheat starch* made into a paste with 1200 of water, and left in a covered but not air-tight saucer for two years; a gray, mouldy, inodorous, semifluid paste, not acid, remained, which, dried at 212°, yielded the above results. B is a similar experiment, in which the starch-paste was kept for thirty-eight days, in a well-corked phial containing a little air. C, the same as B, but air freely admitted. D, a similar paste of *potato starch*, left for forty-two days in a bottle, with a tube cemented into it for carrying off gas: a little hydrogen and carbonic acid were evolved. E, the same as D, but freely exposed. F, the starch paste as above, left for forty days in a glass vessel filled with carbonic acid. The term *amidine*, in the above table, is applied "to a substance intermediate between gum and starch;" and *ligneous starch* to a product insoluble in boiling water and in many acids, but still becoming purple with iodine. The *carbonaceous lignine* gives a brown color to the respective solutions. The influence of carbonic acid in preventing the decomposition of starch is strikingly shown by the contents of the last column. If *gluten* be present, starch begins to pass into sugar in a few hours.

The facility with which sugar is sometimes formed, in consequence apparently of the mere action of air on certain organic principles, is shown in the change which the pulp of many apples undergoes when exposed to air, becoming brown, and at the same time much sweeter. This character belongs to the apples which are preferred for *cyder*, and is obvious by the rapid alteration of color which they exhibit when cut through so as to expose the interior.

3. But the most remarkable conversion of starch into dextrine (and ultimately into sugar) is that which is effected by a peculiar azotised principle to which the term *diastase* has been applied, and which is produced in germinating seeds, and in buds during the period of their development: it is to the presence of this substance that the change of the amylaceous part of the seed into gum and sugar during a certain period of its growth is owing, and it is in consequence of the presence of diastase in *malt*\* that

\* *Malt* is barley which has been made to germinate to a certain extent, after which the process is stopped by heat. The barley is steeped in cold water, and is then made into a heap, or *couch*, upon the malt-floor: here it absorbs oxygen, and evolves carbonic acid; its temperature augments, and

then it is occasionally turned, to prevent its becoming too warm. In this process the *radicle* lengthens, and the *plumula*, called by the maltsters *acrospire*, elongates; and when it has nearly reached the opposite extremity of the seed, its further growth is arrested by drying at a temperature slowly elevated

the brewer's *sweet worts* are produced, and that the addition of an infusion of malt to one of unmalted grain is capable of converting a large proportion of its starch into fermentable matter.

*Diastase* (from *δυστημι*, *I separate*) was first obtained from barley malt by Payen and Persoz. (*Ann. Ch. et Ph.*, liii. 73.) It may be procured from brewers' malt, but in greater quantity from germinated barley carefully prepared for the purpose, in which the germ has been allowed to attain about the length of the seed. The malt is pulverized and macerated in, or triturated for a few minutes with, water, at the temperature of 70° or 80°; the pasty mixture is then strongly pressed, and the turbid liquor which runs from it filtered; the filtrate is then heated in a water bath to about 170°, at which temperature the greater part of the foreign azotized matter coagulates and may be separated by filtration, and the clear filtered liquor retains the diastase and may be used for many purposes as a solution of that substance; it however also retains other principles from which it may be to a great extent separated by the addition of anhydrous alcohol, which forms a flocculent precipitate of diastase insoluble in that liquid; it may be collected and carefully dried at a low temperature, for when heated in a moist state above 190°, its properties are materially altered. It may be further purified by a second solution in water and precipitation by alcohol, and if the solutions are brown, animal charcoal may be resorted to as a means of decoloring them.

Diastase may also be obtained without the aid of heat, but the process requires caution: it consists in triturating the finely-ground malt as before with a little water, pressing out the liquor, and carefully adding a little alcohol to it so as to coagulate its albuminous contents without precipitating the diastase; it is then filtered, and the diastase is separated by the further addition of strong alcohol: it may be purified by a second aqueous solution and alcoholic precipitation, and should be dried at a temperature not exceeding 100°, or in vacuo. It is white, soluble in water and in dilute alcohol, but insoluble in strong alcohol: its aqueous solution is tasteless, and soon becomes sour and decomposes: its effect upon starch is entirely destroyed by boiling: it contains nitrogen, but its ultimate composition has not been accurately determined.

to 150° or more. The malt is then cleansed of the rootlets. According to Dr. Thomson, barley loses about 8 per cent. by converting it into malt, of which

1·5 is carried off by the steep-water.  
3·0 dissipated on the floor.  
3·0 roots separated by cleansing.  
·0·5 waste.

8·0

The following are his comparative analyses of unmalted and malted barley, showing the changes which have taken place in the operation.

|              |    |       |    |
|--------------|----|-------|----|
| Gum .....    | 5  | ..... | 14 |
| Sugar .....  | 4  | ..... | 16 |
| Gluten ..... | 3  | ..... | 1  |
| Starch ..... | 88 | ..... | 69 |

100 barley 100 malt.

According to Proust (*Ann. de Ch. et Ph.*, v. 337), barley also contains a peculiar substance, insoluble in hot water, which he calls *hordein*, and which, during malting, is diminished in quantity, and converted into sugar or starch. Hitherto *hordein* appears to have been confounded with starch. The following are his comparative analyses:—

|              | In 100 of Barley. | In 100 of Malt. |
|--------------|-------------------|-----------------|
| Resin .....  | 1                 | ..... 1         |
| Gum .....    | 4                 | ..... 15        |
| Sugar .....  | 5                 | ..... 15        |
| Gluten ..... | 3                 | ..... 1         |
| Starch ..... | 32                | ..... 56        |
| Hordein .... | 55                | ..... 12        |
|              | 100               | 100             |

The *starch* of malt also differs in some of its properties from that of barley.



Although diastase thus prepared cannot be regarded as a perfectly pure substance it nevertheless possesses a remarkable power of converting starch into dextrine and sugar; to such an extent, indeed, that 1 part of it is capable of thus modifying 2000 parts of starch. Its effect may be well illustrated by adding a minute portion of it to a mixture of 1 part of starch and 8 or 10 parts of water, and then gradually heating it up to between  $160^{\circ}$  and  $180^{\circ}$ : the liquor never acquires the usual consistency of starch paste, but remains a thin fluid containing dextrine and sugar; the latter may be removed by dilute alcohol, and the dextrine remains mixed with any accidental impurities which might have been contained in the starch. If the starch is previously gelatinised by hot water, the action of the diastase is even more rapid, and when complete, all the texture of the starch is entirely destroyed, its chemical peculiarities have disappeared, the liquor contains dextrine and sugar, and the only residuary matter is a little cellular fibre, traces of albumen, and of carbonate and phosphate of lime and silica: of these the proportion varies with the kind of starch, from about a hundredth to a thousandth part of its weight. Guérin has made some experiments to determine the influence of temperature upon the action of diastase. (*Ann. Ch. et Ph.*, LX. and LXI.) He found that at  $68^{\circ}$ , 77.64 parts of sugar were produced by 12.25 of diastase, from 100 of starch paste: at  $32^{\circ}$ , the paste is liquified, and 12 *per cent.* of sugar produced in it; and even at lower temperatures, namely between  $15^{\circ}$  and  $20^{\circ}$ , starch paste is liquified by diastase; but in this case, dextrine only, and no sugar, is the result.

4. Another mode of converting starch into dextrine and sugar is by the protracted action of dilute acids at a high temperature. This conversion was discovered by Kirchoff, of Petersburg, not accidentally, but in consequence of Napoleon's exclusion of colonial produce from Russia, during the enforcement of what was termed the *Continental System*: his ingenuity was rewarded by the Emperor of Russia, with an annuity of 1000 rubles. His method consisted in boiling with very dilute sulphuric acid. A pound of starch may be digested in 6 or 8 pints of distilled water, rendered slightly acid by 2 or 3 drachms of sulphuric acid. The mixture should be simmered for a few days, fresh portions of water being occasionally added to compensate for the loss by evaporation. After this process, the acid is saturated by a proper proportion of chalk, and the mixture filtered and evaporated to the consistence of syrup; its taste is sweet, and by purification in the usual way, it affords *granular* sugar. Dr. Tuthill digested a pound and a half of *potato starch* (obtained from about 9 pounds of potatoes) in a mixture of 6 pints of distilled water, and a quarter of an ounce (by weight) of sulphuric acid, at a boiling heat; the mixture was afterwards stirred, and fresh water occasionally added to supply loss by evaporation. After thirty-four hours an ounce of powdered charcoal was added, and the boiling resumed for two hours. The acid was then carefully saturated by lime, and the boiling continued for half an hour, when the liquor was strained through calico. The insoluble residue, after having been washed and dried, consisted of charcoal and sulphate of lime. The filtered liquor was evaporated to the thickness of syrup; and being set aside, became, in eight days, a crystallized mass, resembling brown sugar and treacle. The sugar weighed one pound and a quarter. One pound of it, fermented in the usual way,

afforded, on distillation, 14 drachms of proof-spirit. (*Nicholson's Journal*, xxxiii.) MM. de la Rive and Saussure have shown that the contact of air is unnecessary in the above process; that no part of the acid is decomposed, no gas evolved, and that the actual sugar obtained exceeds, by about one-tenth, the original weight of the starch. Hence Saussure concludes that the conversion of starch into sugar depends upon the solidification of water, a conclusion borne out by the comparative analyses. Nitric or hydrochloric acid may be substituted in the above process for sulphuric; and among vegetable acids, oxalic, tartaric, and citric acid are effective. When 4 parts of potato starch, 20 of water, and 1 of oxalic acid are boiled together, the mixture becomes thin and limpid in ten minutes, and if this boiling be then continued for five or six hours, or till a small portion of the liquid neutralised with chalk and filtered gives no precipitate with diacetate of lead, the conversion of the starch will be complete: chalk is then added to remove the acid, and the solution boiled, filtered, digested with animal charcoal, and again filtered, evaporated in a water-bath to the consistence of honey, and put aside in a warm place, solidifies into a crystalline mass of grape sugar, perfectly sweet and unaccompanied by any bitterness: the sugar obtained by sulphuric acid is bitter and more difficultly crystallisable. (SPENCER, *Pharm. Journ.*, v. 39.) The properties of the sugar obtained in these processes are in almost all cases identical with those of grape sugar, or glucose, and are elsewhere detailed.

*Dextrine*, as obtained by heating starch, or by Payen's process above described, is either of a pale buff color, or nearly colorless; it has a slight but peculiar odor and flavor; it dissolves in cold and hot water, but is insoluble in alcohol, and not blued by iodine. When its aqueous solution is carefully evaporated, it leaves a hydrated dextrine, amorphous, and somewhat resembling common gum: its ultimate constitution is precisely that of starch, namely,  $C_{24}H_{20}O_{20}$ . It is a valuable substitute for gum, and is often preferable, as remaining more flexible and less brittle when dried: it is largely used in various manufactures; it is applied to the back of the post-office stamps, and is employed for stiffening surgical bandages.

**USES OF STARCH.** Starch is employed for stiffening various fabrics, and articles of wearing apparel\*. In applying it to muslin, the addition of borax or of phosphate of soda, or phosphate of ammonia, would at the same time render it so far incombustible, as to prevent burning with flame, and obviate the accidents that so frequently ensue from that cause. A little smalt, Prussian blue, or indigo, is generally added to starch to cover its yellowish hue, and to render it more effective in overcoming the tinge that linen and cotton acquire when long worn. In this country, the consumption of starch, though considerable, is trifling compared with that in Holland and some other parts of the continent of Europe, where

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\* Potato starch is said to be much more hygrometric than wheat starch, and goods which are stiffened with it, are apt to *give* in damp weather, and to become mouldy if laid by. The thin and cheap calicos are often largely imbued with starch to make them appear of better substance than they really are; this is easily detected by iodine, the vapor or solution of which immediately blues them.



stiffly-starched caps and gauzes are much worn by the lower orders: since the abolition of the absurd custom of powdering the hair, there has also been a great falling off in the demand for starch.

Lozenges, and various articles of confectionery, consist partly of starch; and the sugar-plums, sold in the streets, are composed of the refuse parts of the starch mentioned in describing its manufacture, with chalk, gypsum, and other trash: a spurious *refined liquorice* is also made upon the same principle. *Stone-blue* is a compound of indigo or Prussian blue and the inferior kinds of starch. Among the substances used to adulterate starch, porcelain-clay was at one time prevalent. Considered as an article of food, as a part of the diet of children and of invalids, and as a component of our most nutritious vegetables, starch is very important, and several of its varieties are often resorted to medicinally. But, although eminently adapted to form part of our food, it is not fitted for exclusive nutriment, and this is the case with all those proximate principles of vegetables which are deficient in nitrogen: it is an aliment of respiration, rather than of nutrition.

### § III. SUGAR.

CANE SUGAR. GRAPE SUGAR. HONEY. MANNITE. LIQUORICE SUGAR.  
MUSHROOM SUGAR. ERGOT SUGAR.

SUGAR may be extracted from the juice of a number of vegetables, and is in fact contained in all those having a *sweet* taste. There are two leading varieties of sugar, one of which is familiar to us as the produce of the *Arundo saccharifera*, or *sugar cane*, and the other, as contained in *grapes*, *figs*, *plums*, and fruits in general. The former variety is characterized by the facility with which it crystallizes, and its pure and powerful sweetness: it is also found in beet-root, in the sap of certain species of maple, in the stems of maize, and in some other vegetables, and may be distinguished by the generic term *crystalline* or *cane sugar*. The latter variety of sugar is difficultly and imperfectly crystallizable, and is usually obtained in a granular state, and is of much inferior sweetness: it abounds in grapes, figs, plums, and many other fruits and vegetables, the juices of which are more or less acid: it may also be artificially produced by the action of various agents upon cane sugar, and upon lignin, starch, and gum: it may be distinctively designated *granular* or *grape sugar*; the generic term *glucose* has also been applied to it. There are other important characteristic distinctions between these modifications of sugar, which will afterwards be pointed out. Besides these there are some peculiar sweet principles to which the term *sugar* has been applied, such as that of *manna*, of *liquorice root*, and a few others, which will require separate notice.

CRYSTALLIZABLE OR CANE SUGAR. The manufacture of sugar consists in isolating the concrete sugar from the substances with which it is associated in *cane-juice*, the principal components of which are, water, sugar, gum, albumen, and acetic and malic acids, together with acetate of lime, acetate of potassa, malate of lime, and sulphate of lime.

The following is an outline of the process: The cane, when ripe, is cut off at the root, stripped of leaves and ends, then passed twice through

the mill, so as to express the juice. To prevent fermentation, a portion of lime (about 1 to 1600) is immediately mixed with the juice, which is then passed through a series of boilers or evaporating vessels. In the last of these, called a *teache*, the syrup is boiled until it granulates, or to *proof*, and is then transferred into coolers for the crystals to form and separate from the uncrystallizable portion which has been changed by the action of heat, and becomes *molasses* or *treacle*. The brown crystalline sugar is then packed into hogsheads for exportation, under the name of *muscovado* or *raw sugar*. During this process, the color of the saccharine matter is darkened, and its power of crystallization weakened.

It is said that when the sugar cane has attained its full maturity for grinding, little or no coloring matter is contained in a soluble state in the juice, but that it exists combined with the waxy or resinous particles forming the green deposit which is precipitated by the lime, and that during boiling, the lime again renders this matter soluble, and so deteriorates the sugar.

As regards the *treacle*, Dr. Turner observes that "its saccharine principle has been supposed to be different from crystallizable sugar; but it consists chiefly of common sugar, which is prevented from crystallizing by the presence of foreign substances, such as saline and other vegetable matters." And there can be no doubt that during boiling, and in consequence of the foreign matters present, a portion of the crystallizable sugar has been converted into granular sugar.

The process of *refining sugar* consists in separating the pure crystals from the uncrystallizable and coloring matter contained in raw or muscovado sugar. The following is a sketch of this process.

Raw sugar is chosen for the purpose of refining by the sharpness and brightness of the grain, and those kinds are preferred which have a peculiar grey hue. Soft-grained yellow sugars, although whiter, are not so fit for refining, and it is for this reason that sugars from particular colonies are seldom used, such as those from the East Indies, Barbadoes, &c.

The proper sugar being selected, the *pans* are charged with a certain portion of lime water, with which bullocks' blood is well mixed by agitation. They are then filled with the sugar, which is suffered to stand a night to dissolve. The use of the lime water is to render the molasses more soluble, and thus to facilitate its separation from the crystallizable sugar. With the purer kinds of sugar, and more especially when refined sugar is re-dissolved for the purpose of bringing it to its utmost degree of purity, lime is not used, the quantity of molasses being so small as to be easily removed by the agency of water alone.

Fires are lighted under the pans early in the morning, and when the liquid begins to boil, the albumen of the blood coagulates and rises to the top, bringing the impurities of the sugar with it. These are taken off with a skimmer. The liquid is kept gently simmering and continually skimmed, till a small quantity, taken in a metallic spoon, appears transparent: this generally takes from four to five hours. The whiteness of the sugar is not improved by this process, but even sometimes deteriorated, from the action of the fire; it only serves to remove foreign impurities.

The *color* (as the refiners term it) or *whiteness* of the sugar when refined, depends in a great measure on the quantity of animal charcoal used in this part of the process. It is applied frequently to the first



solution of the sugar and water. In some refining-houses the solution is filtered through beds of animal charcoal. The solution is, when perfectly bright and clear, run off into a large cistern.

The pans are then reduced to half their size by taking off their fronts, and a quantity of syrup returned into each, which is made to boil as rapidly as possible, till it is capable of being drawn into threads. Nothing but practice can ascertain the exact point at which the boiling should be stopped: if carried too far, the molasses is again bound up with the sugar; and if not carried far enough, much of the sugar runs off with the molasses in the after-process. When this point is ascertained, the fire is damped, and the boiling sugar carried to the *coolers*: a fresh quantity is then pumped into the pans, which is evaporated as before.

When the sugar is in the coolers, it is agitated with wooden oars till it appears granulated, and is no longer capable of being drawn into threads. It is upon this agitation in the cooler that the whiteness and fineness of grain in the refined sugar depend. The crystals are thus broken whilst forming, and the whole converted into a granular mass, which permits the colored liquid saccharine matter to run off, and which would be combined with the solid, if suffered to form in larger crystals. This granular texture likewise facilitates the percolation of water through the loaves in the after-process, which washes the minutely-divided crystals from all remaining molasses. That this is the true theory of the whitening of sugar by the process of refining, appears from a comparison with the process of making *candy*. In this latter, the raw material is cleared and boiled exactly in the same manner; but instead of being put into coolers and agitated, it is poured into pots, across which threads are strung, to which the crystals attach themselves; these are set in a stove, and great care is taken not to disturb the liquid, as upon this depends the largeness and beauty of the candy. In this state it is left for five or six days, exposed to a heat of about  $95^{\circ}$ , when it is taken out and washed with lime water: this takes off the molasses from the outside, but a portion is combined in the crystals, and the consequence is, that candy is never whiter than the sugar from which it is made.

When the sugar has arrived at that granular state in the coolers, above described, it is poured into conical earthen moulds, which have previously been soaked a night in water. In these it is again agitated with sticks, for the purpose of extricating the air-bubbles which would otherwise adhere to the sugar and the moulds, and leave the coat of the loaf rough and uneven. When sufficiently cold, the moulds are taken to the upper floors of the manufactory, and the paper stops being removed from their points, they are set, with their broad ends upward, upon earthen pots. The first portions of the liquid molasses soon run down, and leave the sugar whitened by the separation. This self-clearance is assisted by a high temperature; and when it is perfected, pipe clay, carefully mixed with water to the consistence of cream, is put upon the base of the loaves to the thickness of about an inch: the water from this slowly percolates them; and, washing the solid sugar from all tinge of molasses, runs into the pots. The clay is of no other use than to retain the water, and prevent its running too rapidly through the mass, by which too much of the sugar would be dissolved; a sponge, dipped into water, acts in the same manner. The process of *claying* is repeated four or five

times, according to the nature of the sugar, and the degree to which it has been boiled. When the loaves are cleansed from all remains of the colored fluid, they are suffered to remain some time for the water to drain off; when this is completed, they are set with their bases downwards, when all remains of it return from their points, and it is equally diffused throughout: they are then set in a stove, heated to about  $95^{\circ}$ , and thoroughly dried.

The *syrup*, or the mixed solution of sugar and molasses which runs into the pots, is mingled in the next boilings with the solution of raw sugar in the pans, and again evaporated. It is divided according to its fineness; the first running, containing most molasses, is reserved for the coarser loaves; whilst the last, being little else than a solution of sugar, is boiled into loaves, of the same degree of fineness as those from which it ran. The lowest syrups are boiled into what is called *bastard sugar*, from which the molasses runs with very little mixture of the solid sugar. This is called *treacle*, and is incapable of further crystallization.

The average produce of 1 cwt. of good raw sugar worked in this manner, is 63 lbs. refined, 18 lbs. bastard, 27 lbs. molasses, 4 lbs. lost weight, dirt, &c.

The process above described may almost be considered as mechanical; the only chemical parts of it being the clearing with blood, and the use of lime water, which, combining with the molasses, facilitates its solution during the percolation of the water.

It cannot be doubted that much improvement may be made in refining sugar, by the aid of chemistry, so as to produce a larger quantity of *refined* from *raw sugar*, by extracting all the foreign matters remaining in the raw sugar, and which, when again exposed to high temperatures, in the process of refining, further decompose the saccharine matter. The plan of refining by open pans is now nearly superseded by the application of steam, and by Howard's plan of evaporating *in vacuo*, or at least under a greatly-diminished atmospheric pressure, by which, exposure to any temperature liable to injure the sugar, is effectually prevented. The process of *claying* is also now sometimes omitted, and water is suffered to drop upon the base of the loaf; or in some cases a strong solution of pure sugar is substituted, upon the principle that water, having a stronger affinity for the molasses, than for the solid sugar, will, in percolating the crystals, dissolve the molasses, and leave the sugar to enlarge and aggregate the crystals, rendering the *loaves* of more weight and closer grain; but in this case there is a difficulty in getting the viscid syrup to pass through the saccharine filter. Filters of animal charcoal are now employed in all sugar refineries, as an auxiliary means of decoloring the syrups; hydrated alumina has also been used for a similar purpose.

In making the saccharine solutions as well as in their subsequent evaporation, it is obviously desirable to avoid such elevation of temperature as may in any way tend to discolor or decompose them, and high-pressure steam, oil, and various saline solutions, have accordingly been resorted to as media for the communication of heat. The object is in all cases to boil and evaporate, without elevating the temperature to that point at which cane sugar suffers change. According to Dr. Henry, "a mixture of 1 part of water and 3 of sugar boils rapidly at  $230^{\circ}$ ; and from this to  $240^{\circ}$  is its due temperature. If a solution of sugar be further concentrated by



the evaporation of water, the thermometer rises to  $340^{\circ}$ . The sugar then begins to turn black, and at  $370^{\circ}$  it takes fire on applying flame to its vapor, and burns strongly, leaving a residuum of charcoal." Ample details of all that relates to the manufacture and produce of sugar, are given by Dumas, (*Chim. app. aux Arts*, vi. 209;) and by Ure, (*Dictionary of Arts, &c.*)

It has already been stated that a sugar, identical with that from the sugar cane, may be extracted from *beet root*, and from the sap of the *sugar maple*.

*Beet Sugar* is obtained from the *Beta vulgaris*. The manufacture of sugar from beet root has long been successfully and extensively pursued in France: many interesting details respecting it will be found in a paper in the *Quarterly Journal*, xxi. 252; and the process of its manufacture, together with the apparatus employed, is described at length by Dumas. (*Chim. app. aux Arts*, vi. 145.) The roots, having been softened in water, are sliced, and the juice is expressed and boiled down to about two-thirds its bulk, with the addition of a little lime; it is then strained, again evaporated, and purified in the same way as cane sugar. 100 lbs. of the root furnish between 4 and 5 lbs. of purified white sugar, besides a quantity of syrup, at the average expense (in France) of between three-pence and fourpence a pound.

*Maple Sugar* is the produce of the *Acer saccharinum*, which is cultivated as a source of sugar in North America, especially in the states of New York and Pennsylvania, where it is said to yield a larger proportion of sugar than that which grows upon the Ohio. A hole is bored through the bark into the alburnum, in spring, from which the sap flows to such an extent, that a tree of average size yields about 50 quarts in 24 hours; it contains 5 *per cent.* of sugar. The sap is collected during five or six weeks: it is rapidly boiled down, and yields a coarse sugar, which, however, may be purified by the same processes as cane sugar, and resembles it in its properties.

*Indian Corn Sugar.* The stalks of *Zea Mays*, especially when the ears of corn have been removed as they begin to form, yield as much sugar as the ordinary cane: 6 quarts of the juice gave a quart of syrup containing 16 *per cent.* of sugar. (H. CROFT, *Chem. Gaz.*, Mar. 1843.) According to Biot and Soubeiran, the produce of crystalline sugar is about 10 to 11 *per cent.* Carrots, turnips, and *Spanish chesnuts*, also contain cane sugar.

CANE SUGAR is a white brittle substance of a pure sweet taste. It is phosphorescent on friction. Its specific gravity is about 1.5 to 1.6. It is dissolved by about one-third of its weight of cold water, and boiling water dissolves a considerably larger quantity, but the solubility of sugar in water of different temperatures, has not been accurately determined: according to Wenzel (*Verwandschaft*, p. 308), water at  $48^{\circ}$  dissolves its own weight only of pure sugar. Its usual crystalline form is that of a six-sided prism, which is generally flattened and irregularly terminated. (GILLOT, *Ann. de Chimie*, xviii. 317.) The following table of the specific gravity of solutions of cane sugar of different strengths at the temperature of  $63^{\circ}$  has been constructed by Niemann. (*Ann. der Pharm.*, II. 340.)

| Sugar. | Water.   | Sp. gr.     | Sugar. | Water.  | Sp. gr.     | Sugar. | Water.  | Sp. gr.     |
|--------|----------|-------------|--------|---------|-------------|--------|---------|-------------|
| 0      | .... 100 | .... 1·0000 | 24     | .... 76 | .... 1·1010 | 48     | .... 52 | .... 1·2209 |
| 1      | .... 99  | .... 1·0035 | 25     | .... 75 | .... 1·1056 | 49     | .... 51 | .... 1·2265 |
| 2      | .... 98  | .... 1·0070 | 26     | .... 74 | .... 1·1103 | 50     | .... 50 | .... 1·2322 |
| 3      | .... 97  | .... 1·0106 | 27     | .... 73 | .... 1·1150 | 51     | .... 49 | .... 1·2378 |
| 4      | .... 96  | .... 1·0143 | 28     | .... 72 | .... 1·1197 | 52     | .... 48 | .... 1·2434 |
| 5      | .... 95  | .... 1·0179 | 29     | .... 71 | .... 1·1245 | 53     | .... 47 | .... 1·2490 |
| 6      | .... 94  | .... 1·0215 | 30     | .... 70 | .... 1·1293 | 54     | .... 46 | .... 1·2546 |
| 7      | .... 93  | .... 1·0254 | 31     | .... 69 | .... 1·1340 | 55     | .... 45 | .... 1·2602 |
| 8      | .... 92  | .... 1·0291 | 32     | .... 68 | .... 1·1388 | 56     | .... 44 | .... 1·2658 |
| 9      | .... 91  | .... 1·0328 | 33     | .... 67 | .... 1·1436 | 57     | .... 43 | .... 1·2714 |
| 10     | .... 90  | .... 1·0367 | 34     | .... 66 | .... 1·1484 | 58     | .... 42 | .... 1·2770 |
| 11     | .... 89  | .... 1·0410 | 35     | .... 65 | .... 1·1538 | 59     | .... 41 | .... 1·2826 |
| 12     | .... 88  | .... 1·0456 | 36     | .... 64 | .... 1·1582 | 60     | .... 40 | .... 1·2882 |
| 13     | .... 87  | .... 1·0504 | 37     | .... 63 | .... 1·1631 | 61     | .... 39 | .... 1·2933 |
| 14     | .... 86  | .... 1·0552 | 38     | .... 62 | .... 1·1681 | 62     | .... 38 | .... 1·2994 |
| 15     | .... 85  | .... 1·0600 | 39     | .... 61 | .... 1·1731 | 63     | .... 37 | .... 1·3050 |
| 16     | .... 84  | .... 1·0647 | 40     | .... 60 | .... 1·1781 | 64     | .... 36 | .... 1·3105 |
| 17     | .... 83  | .... 1·0698 | 41     | .... 59 | .... 1·1832 | 65     | .... 35 | .... 1·3160 |
| 18     | .... 82  | .... 1·0734 | 42     | .... 58 | .... 1·1833 | 66     | .... 34 | .... 1·3215 |
| 19     | .... 81  | .... 1·0784 | 43     | .... 57 | .... 1·1935 | 67     | .... 33 | .... 1·3270 |
| 20     | .... 80  | .... 1·0830 | 44     | .... 56 | .... 1·1989 | 68     | .... 32 | .... 1·3324 |
| 21     | .... 79  | .... 1·0875 | 45     | .... 55 | .... 1·2043 | 69     | .... 31 | .... 1·3377 |
| 22     | .... 78  | .... 1·0920 | 46     | .... 54 | .... 1·2098 | 70     | .... 30 | .... 1·3430 |
| 23     | .... 77  | .... 1·0965 | 47     | .... 53 | .... 1·2153 |        |         |             |

The aqueous solution of sugar, or *syrup*, is viscid, and when sufficiently concentrated deposits part of its sugar in the form of crystals, or *candy*, composed, according to Berzelius, of 100 sugar + 5·6 water. A solution saturated at 230° concretes, on cooling, into a granular mass or *tablet*, but when the syrup is rapidly boiled down till it acquires a tendency to vitreous fracture on cooling, or till a portion thrown off from a stirrer concretes or *feathers* as it falls, it congeals when poured out upon a marble or metallic plate into a transparent amorphous mass, commonly called *barley sugar*, which gradually becomes opaque, and passes into a fibrous or granular crystalline texture; so that sugar presents a case of dimorphism somewhat analogous to that of sulphur. To prevent or retard this opacity from crystallization, confectioners add a small quantity of vinegar, or of tartaric acid, to the sugar. When syrup is long kept at a temperature near its boiling-point, it loses its tendency to crystallization, in consequence, probably, of its partial conversion into glucose. Sugar is soluble in alcohol, but more sparingly so than in water; when of the specific gravity of ·830, it takes up about one-fourth its weight of pure white sugar; but absolute alcohol dissolves only about one-eightieth of its weight at its boiling-point, and on cooling, almost the whole separates in small crystals. When equal parts of strong syrup and alcohol are mixed, a quantity of small brilliant crystals of sugar are soon deposited.

Pure sugar is unchanged by air, and perfectly-pure syrup is not prone to change; but the addition of certain other substances, though in very minute quantity, materially influences the stability of this solution. These, and other changes of such mixtures, we shall consider under the article *Fermentation*.

When sugar is exposed to a heat of 212° it undergoes no other change than that occasioned by the loss of adhering water; but at 300° it begins to fuse, becomes brown or black, evolves a little water, and is





|             | A      |      | B C    |      | D      |      | E      |      | F G    |      | H      |
|-------------|--------|------|--------|------|--------|------|--------|------|--------|------|--------|
| Carbon .... | 42.85  | .... | 42.00  | .... | 41.90  | .... | 42.20  | .... | 42.10  | .... | 40.88  |
| Hydrogen .. | 6.35   | .... | 6.44   | .... | 6.46   | .... | 6.42   | .... | 6.43   | .... | 6.57   |
| Oxygen....  | 50.80  | .... | 51.56  | .... | 51.64  | .... | 51.38  | .... | 51.47  | .... | 52.55  |
|             | <hr/>  |      | <hr/>  |      | <hr/>  |      | <hr/>  |      | <hr/>  |      | <hr/>  |
|             | 100.00 |      | 100.00 |      | 100.00 |      | 100.00 |      | 100.00 |      | 100.00 |

A Purified candy; B West India candy; C English refined; D East India candy; E East India refined; F Maple sugar; G Beet sugar; H East India moist.

**ACTION OF ACIDS ON CANE SUGAR.** This is complicated, and varies with their state of concentration and the facility with which they are decomposed, and impart oxygen.

*Concentrated sulphuric acid* energetically decomposes sugar, evolving charcoal, and forming water, formic acid, and some other products. It is a striking experiment to mix about equal bulks of strong syrup and sulphuric acid; the mixture, when stirred, presently becomes brown and black, then suddenly heats, boils up, and passes into the state of an almost solid and very bulky magma of charcoal: the acid appears suddenly to abstract from the sugar the elements of water.

When cane sugar is dissolved in very *dilute sulphuric acid* and boiled, it is gradually altered and converted into that modification of sugar which is obtained by the action of the same acid upon starch, namely, into *glucose* or *grape sugar*. The same effect is produced by *hydrochloric* and several other acids; and if the boiling be long continued, the liquor becomes brown in consequence of the formation of what has been termed *sachulmine* or *sachulmic acid*: these are brown or black uncrystallizable products formed in a variety of other cases, in which acids and alkalis are made to act, under particular conditions, upon several organic products, and which are also generated during their decay: they will be more especially described afterwards. *Nitric acid*, when extremely dilute, produces changes similar to the preceding; but when stronger, its action is attended by the production of saccharic and oxalic acids, and ultimately these are resolved into carbonic acid and water.

The action of chlorine, iodine, and bromine upon sugar has not been minutely examined; dry chlorine does not act on dry sugar, but it is

On these Dr. Prout makes the following remarks: "The *sugar-candies* of the shops frequently contain minute quantities of foreign fixed bodies, such as lime, &c., as well as others of a destructible character. Both the specimens of *India sugar-candy* I examined were obviously impure to the eye, being of a brown color, and deliquescent; they contained, among other things, traces of potash. The *East India refined sugar* was perfectly white, but rather soft and friable, and it did not possess the fine and brilliant grain of the best refined sugars of commerce. For a specimen of the *maple sugar* I was indebted to Mr. Faraday; this, when I received it, was very impure and deliquescent, but by treating it by the process above alluded to (see *Phil. Trans.*), a

portion was separated that differed but little in its appearance from cane sugar. The *beet root sugar* was made and refined in France; it was perfectly white, but rather soft and fine in the grain. The *East India moist sugar* was of a very low kind, and known in commerce by the name of *Burdwan sugar*; it was deprived of its hygrometric moisture before analysis by exposure to sulphuric acid under a receiver. The *diabetic sugar* was prepared as above; the results given were obtained many years ago, and I have had no opportunity of repeating the analysis with the present apparatus; I believe, however, that diabetic sugars, in general, belong to the honey variety. The *sugar of starch* was prepared by myself in the usual manner."



absorbed by syrup, and hydrochloric acid and a brown matter are produced.

*Arsenic acid* renders syrup pink, purple, and brown, and the odor of acetic acid is evolved. When this saccharine solution of arsenic acid is decomposed by sulphuretted hydrogen, a yellow sweet liquid remains, not precipitated by acetate of lead.

**ACTION OF BASES ON CANE SUGAR.** Sugar absorbs gaseous ammonia, and forms with it, according to Berzelius, a definite compound, containing 90.28 sugar, 4.72 ammonia, and 5.00 water, or 1 atom of sugar, 1 of ammonia, and 1 of water, but which, exposed to air, loses ammonia and leaves unaltered sugar. Sugar dissolves in solutions of potassa and soda, losing its sweetness, and yielding on evaporation a product insoluble in alcohol, but which, if accurately neutralized by dilute sulphuric acid, yields unaltered sugar, which may be separated by alcohol. (BERZELIUS.)

The hydrated alkaline earths are soluble in large proportion in syrup. When the solutions are evaporated, uncrystallizable gumlike compounds remain, insoluble in alcohol. From a solution of sugar and lime, Daniell obtained crystals of carbonate of lime, and a gummy substance. The addition of phosphuret of lime to syrup produced an analogous change. (*Journal of Science and the Arts*, vi. 32.) According to Peligot (*Ann. Ch. et Ph.*, LXXII. 113,) hydrate of lime dissolves in solution of sugar, and forms a bitter liquor, from which alcohol throws down a definite compound (*saccharide of lime*) containing between 14 and 15 *per cent.* of lime: it forms a brittle amorphous substance when dried. When its cold aqueous solution is heated, it soon becomes opalescent, and afterwards deposits flakes of the saccharide resembling albumen, and which are insoluble in boiling water, but they dissolve again in cold water, so that the opaque hot solution returns to its transparency as it cools: this is a remarkable case of solubility in cold, but insolubility in hot water. This compound is  $= \text{CaO}, \text{HO} + \text{C}_{12} \text{H}_{19} \text{O}_9$ : its components being

|                         |   |     |     |     |       | Peligot. |
|-------------------------|---|-----|-----|-----|-------|----------|
| Lime .....              | 1 | ... | 28  | ... | 14.7  | 14.2     |
| Water .....             | 1 | ... | 9   | ... | 4.8   | 85.8     |
| Anhydrous sugar.....    | 1 | ... | 153 | ... | 80.5  |          |
| <hr/>                   |   |     |     |     |       |          |
| Saccharide of lime .... | 1 |     | 190 |     | 100.0 | 100.0    |

Sugar also forms a definite compound with baryta  $= \text{BaO}, \text{HO}, \text{C}_{12} \text{H}_{19} \text{O}_9$ . It may be obtained by boiling a mixture of syrup and baryta water, when it is deposited in small crystalline tufts. With concentrated solutions of sugar and baryta a crystalline magma is formed, which heat increases, and which may be washed with cold water by decantation, as it rapidly absorbs carbonic acid from the air. It contains

|                      |   |      |     |      |        | Peligot.  |
|----------------------|---|------|-----|------|--------|-----------|
| Baryta .....         | 1 | .... | 77  | .... | 32.22  | .... 31   |
| Water .....          | 1 | .... | 9   | .... | 3.77   | } .... 69 |
| Anhydrous sugar..... | 1 | .... | 153 | .... | 64.01  |           |
| <hr/>                |   |      |     |      |        |           |
| Saccharide of baryta | 1 |      | 239 |      | 100.00 | 100       |

A boiling solution of sugar dissolves oxide of lead, and on cooling, deposits a white powder, which, when dried at  $212^\circ$ , is an anhydrous compound  $= 2\text{PbO}, \text{C}_{12} \text{H}_{19} \text{O}_9$ . It may be obtained crystallized with 1

atom of water, by mixing syrup with solution of acetate of lead and ammonia; a gelatinous precipitate falls, which, when dissolved in boiling water, deposits crystalline tufts. The anhydrous compound contains

|                        |   |      |     |      |        |
|------------------------|---|------|-----|------|--------|
| Oxide of lead .....    | 2 | .... | 224 | .... | 59.42  |
| Anhydrous sugar.....   | 1 | .... | 153 | .... | 40.58  |
| <hr/>                  |   |      |     |      |        |
| Saccharide of lead.... | 1 |      | 377 |      | 100.00 |

Sugar also forms a crystalline compound with chloride of sodium; it is obtained by dissolving 1 part of the chloride and 4 of sugar in water, and leaving the solution to spontaneous evaporation, after having evaporated it to the consistency of syrup: crystals of sugar are first deposited, but the decanted liquor afterwards yields the compound, in small brilliant crystals, which are very soluble and deliquescent, and therefore difficultly obtained: their taste is both salt and sweet; their formula appears to be  $\text{Na Cl}, 3\text{H}_2\text{O}, 2[\text{C}_{12}\text{H}_{19}\text{O}_9]$ , containing

|                                  |   |      |     |      |        |        |                  |
|----------------------------------|---|------|-----|------|--------|--------|------------------|
| Chloride of sodium .....         | 1 | .... | 60  | .... | 15.26  | ....   | Peligot.<br>14.9 |
| Water .....                      | 3 | .... | 27  | .... | 6.86   | } .... | 85.1             |
| Anhydrous sugar .....            | 2 | .... | 306 | .... | 77.88  |        |                  |
| <hr/>                            |   |      |     |      |        |        |                  |
| Saccharide of chloride of sodium | 1 |      | 393 |      | 100.00 |        | 100.0            |

The compounds of sugar with potassa, lime, and baryta, may be used as sources of other analogous combinations by double decomposition, and in the production of double salts. Alone they exert no solvent power over metallic oxides; and neither syrup, nor the compound of lime and sugar, are separately capable of dissolving hydrated oxide of copper; but if that oxide be added to a mixture of syrup and the lime compound, it readily dissolves and forms a deep blue liquor, which is alkaline, and therefore insensible to the action of the alkalis: it leaves when evaporated in vacuo a blue uncrystallizable compound; it gradually changes when exposed to air, and deposits hydrated suboxide of copper. It is decomposed by sulphuretted hydrogen, and by ferrocyanide of potassium.

This reduction or change of the oxide into suboxide of copper is very speedily effected by boiling the hydrated oxide with grape sugar, and is a useful test of that substance. The best cupreous solution for the purpose is that of tartrate of copper in caustic or carbonated soda; this is a deep blue liquor, which, with the minutest addition of grape sugar, is decomposed at a boiling-heat, and a yellow hydrated dioxide of copper is thrown down, which when collected on a filter, washed, and dried, assumes a red color. Cane sugar, to become sensible to this test, must be previously converted into grape sugar, by boiling its solution with the addition of a few drops of sulphuric acid. When used as a quantitative test, a preliminary comparative experiment should be made, by dissolving a given weight of pure cane sugar in water, boiling it for 15 minutes with the addition of a little sulphuric acid, then mixing it with the alkaline solution of copper, and boiling till the precipitate acquires a red color, when it may be collected, washed, dried, and weighed: in an experiment of this kind, 5 grains of cane sugar treated by sulphuric acid, yielded a precipitate on boiling with the cupreous liquor = 11 grains. A still more delicate test of grape sugar is the liquor obtained by mixing a solution of chloride of platinum with tartaric acid, and adding excess of solution of soda: when the smallest trace of grape sugar is added to this



liquor and the mixture boiled, it blackens, and metallic platinum is thrown down, the weight of which may be resorted to as the indicator of that of the sugar. (L. THOMPSON.)

When sugar is boiled with solution of nitrate of silver, a black powder is formed, which has not been examined: from perchloride of mercury it throws down the protochloride. When syrup is added to the solutions of peroxide of iron, the whole of the oxide cannot be precipitated by ammonia.

**GRANULAR SUGAR. GLUCOSE. GRAPE SUGAR.** It has been already stated, that this modification of sugar, (the *Krümel-zucker* of the German chemists,) exists in the juice of several fruits, and may be produced artificially from cane sugar, starch, and some other substances: it may also be obtained from honey: it forms the saccharine concretions found in raisins, and the saccharine efflorescence upon dried figs, plums, &c. In good seasons the expressed juice of grapes contains from 30 to 40 *per cent.* of solid matter, the greater part of which is this species of sugar: there is a small relative quantity of gum, extractive, gluten, and bitartrate of potassa. To obtain the sugar, the juice is neutralized by the addition of chalk or powdered marble, strained or filtered, mixed with a little white of egg, boiled, skimmed, and evaporated till of the specific gravity of 1.32. It is then allowed to cool, and in a few days it concretes into a solid mass, which is drained, and then dried by pressure; it affords about three parts of dry sugar and 1 of syrup. The sugar may be rendered white by boiling it with charcoal.

The formation of this species of sugar by the action of acids and of diastase upon gum and starch, has already been adverted to. It is in this way largely manufactured, especially in France, where it is sold as an article of commerce. Dr. Pereira states that it is made at Stratford in Essex, and that brown sugar is extensively adulterated with it. Its usual source is potato starch, and sago, which are saccharised by the action of dilute sulphuric acid; (10 parts of acid to 1000 of water and 500 of starch.) The dilute acid is heated by steam to between 212° and 220°; and the starch, previously mixed to about the consistency of thin cream with water of a temperature between 112° and 130°, is then suffered gradually to dribble in under constant stirring; its conversion into dextrine is immediate; in about two hours and a half the whole of the starch is added, and in from 15 to 25 minutes afterwards the saccharification is complete; the steam is then shut off, and the liquor transferred to another vat, so that the first may receive a new charge. In this second vat the acid of the liquor is carefully saturated with powdered chalk thrown in by little at a time to prevent inconvenient effervescence. When the sulphate of lime has subsided, the clear liquid is drawn off and rapidly evaporated to the specific gravity of about 1.26 (30° Baumé): the sulphate is put upon a strainer, and when drained the remaining sugar is washed out of it. The resulting syrup is then left at rest to deposit the sulphate of lime separated during evaporation, and may afterwards be drawn off perfectly clear. In this state it may be used as a source of alcohol, or for sweetening colored liquors, but it requires, for the greater number of purposes, to be deprived of color: for this purpose it is passed whilst hot through filters of coarsely-powdered animal charcoal,

which also improves its flavor. When this sugar is required in its solid form, the syrup is concentrated by evaporation in a steam vat, till it attains the specific gravity of about 1·45 (45° Baumé): this process should be conducted as rapidly as possible to avoid the resumption of a yellow tint: it is then poured into shallow coolers, where it concretes. Dumas, from whom I have abridged this account, describes another form of glucose prepared in Paris, under a patent granted to M. Fouschard: it consists in allowing the whole of the syrup to run off from the granulated sugar, which is afterwards dried upon thick tablets of plaster, at a temperature of about 78°, and pulverised. He observes that during these operations the disagreeable odor of potato oil is frequently evolved to such an extent as to annoy the neighbourhood, which may be avoided by condensing the vapor, so that the heat evolved may be applied to the evaporation of the syrup; the gases, and uncondensed vapor, are conveyed into the fire or chimney. The syrups obtained by the action of *diastase* are not liable to this inconvenience.

The composition of glucose or grape sugar, has been variously represented, but the formula  $C_{12}H_{14}O_{14}$ , or  $C_{24}H_{28}O_{28}$ , is that which is generally assigned to it in its ordinary crystallized state as dried at 212° or in vacuo. Peligot represents this by  $C_{24}H_{21}O_{21} + 7HO$ , assuming the formula  $C_{24}H_{21}O_{21}$ , for anhydrous glucose as it exists in certain states of combination. Crystallized glucose therefore may have the equivalents 198 or 396: in the former case its constituents are

|                                 |    |     |     |     |        | Prout.  | Saussure. |          |        |       |        |
|---------------------------------|----|-----|-----|-----|--------|---------|-----------|----------|--------|-------|--------|
|                                 |    |     |     |     |        | (Honey) | (Grapes)  | (Starch) |        |       |        |
| Carbon .....                    | 12 | ... | 72  | ... | 36·36  | ...     | 36·36     | ...      | 36·71  | ...   | 37·29  |
| Hydrogen ....                   | 14 | ... | 14  | ... | 7·08   | ...     | 7·09      | ...      | 6·78   | ...   | 6·84   |
| Oxygen .....                    | 14 | ... | 112 | ... | 56·56  | ...     | 56·55     | ...      | 56·51  | ...   | 55·87  |
| <hr/>                           |    |     |     |     |        | <hr/>   | <hr/>     | <hr/>    | <hr/>  | <hr/> | <hr/>  |
| Crystallised }<br>glucose.... } | 1  |     | 198 |     | 100·00 | 100·00  | 100·00    |          | 100·00 |       | 100·00 |

Glucose or grape sugar solidifies very slowly from a solution of a proper strength, in fibrous groups, or in small hemispherical tubercles composed of an assemblage of acicular crystals; it may be obtained from its alcoholic solution, in square tables and cubes. Its taste is less agreeably sweet than that of cane sugar, and its sweetening power is so inferior, that 2 parts of cane sugar render a given volume of water quite as sweet as 5 parts of grape sugar. Heated to a little above 212°, it loses about 9 *per cent.* of water, and fuses into a yellow transparent mass, which absorbs moisture from the atmosphere, and at first liquifies, and having regained its 9 *per cent.* of water, it again concretes. At about 285° it becomes converted into caramel, and at higher temperatures is decomposed exactly as cane sugar.

Grape sugar is much less soluble in water than cane sugar. It requires 1·33 parts of cold water for solution, and is a long time before it becomes dissolved: it dissolves more readily and abundantly in hot water, but its syrup never acquires the adhesiveness or viscosity of that of cane sugar; it tastes sweeter than the solid sugar. The pure aqueous solution of this sugar is permanent; but if any ferment be added, it immediately undergoes alcoholic fermentation. Grape sugar dissolves in 20 parts of absolute alcohol, and in 8 parts of alcohol, sp. gr. 0·835; (LIEBIG), but according to Dumas, it is much less soluble in alcohol



than cane sugar. (*Chim. app. aux Arts*, vi. 275.) The crystals which are deposited from its hot alcoholic solution retain alcohol.

**ACTION OF ACIDS ON GRAPE SUGAR.** This differs in many respects from their action on cane sugar. When pure grape sugar is triturated with concentrated sulphuric acid, a solution is obtained which is only slightly colored, and which contains a peculiar acid which has been termed *sulphoglucic* or *sulphosaccharic acid*. (PELIGOT.) This acid may be obtained by fusing 2 parts of grape sugar and 3 of sulphuric acid in a water-bath, constantly stirring the mixture so as to keep down its temperature, and if necessary plunging the vessel containing it into cold water to mitigate the action. The resulting combination is then dissolved in water, and carbonate of baryta added, which occasions the precipitation of sulphate of baryta, while a soluble baryta compound (sulphosaccharate) is retained in solution: this may be decomposed by a solution of basic acetate of lead, by which an insoluble sulphosaccharate of lead is thrown down, and which may be diffused through water, and decomposed by sulphuretted hydrogen. The solution thus obtained (after the expulsion of the excess of sulphuretted hydrogen) is sweetish and slightly acid; it forms a soluble salt with baryta, and with the greater number of other bases; when it is evaporated, even in vacuo, it begins to be decomposed when it attains a certain degree of concentration, and therefore to precipitate the salts of baryta. The formula of this acid is  $C_{24}H_{20}O_{20},SO_3$ . (PELIGOT.) Nitric acid transforms grape sugar into saccharic and oxalic acid. It is rendered at first red and then brown, when mixed with a concentrated solution of arsenic acid.

The protracted action of *dilute acids* on grape sugar is attended by some curious transformations which, perhaps, are best illustrated by using very dilute sulphuric acid. It has already been stated, that when cane sugar is boiled in such an acid, it is gradually converted into grape sugar, and this conversion is attended by the production of a peculiar odor, and the liquor assumes a brownish hue. The time required for the completion of these changes varies with the strength of the acid, and if the boiling be continued, the liquor gradually deposits a brown powder (ulmine and ulmic acid,) and evolves the odor of formic acid, provided air be admitted to it during ebullition. In this way Malaguti found that with 40 parts of sugar candy, 120 of distilled water, and 2 of sulphuric acid, boiled for 24 hours, he obtained about 4.5 of formic acid, 13 of brown matter, and 20 of glucose. When 50 parts of sugar, 150 of water, and 4 of nitric acid, were boiled together for 15 hours in a flask with a very long zig-zag tubular neck to condense the vapor, a deep reddish brown liquor was obtained, containing black shining particles and a brown powder. This deposit increased on prolonging the boiling to 24 hours, and the odor of formic acid became very evident. When 10 parts of sugar, 30 of water, and 1 of sulphuric acid are boiled together in an open basin, in about three-quarters of an hour a brown scum makes its appearance, which when removed is rapidly replaced by fresh formations. When digested in ammonia, this brown acid matter deposits ulmine, and furnishes *ulmate of ammonia*? (MALAGUTI.)

**ACTION OF BASES ON GRAPE SUGAR.** The action of the alkalis on grape sugar differs in its results from those which they produce upon cane

sugar, and when used in excess, and especially when aided by heat, they form with it brown mixtures, which exhale the odor of burnt sugar. With a strong solution of caustic potassa, the sugar soon disappears, and by boiling sugar with a weak solution of potassa for 24 hours, formiate of potassa is gradually produced.

The compound of grape sugar with lime, *glucoside of lime*, is precipitated on the addition of alcohol to a recent solution of slaked lime in syrup of grape sugar; it must be carefully washed with alcohol, and dried in vacuo. It is a deliquescent white compound, but easily rendered brown by heat: when well dried it contains 24.26 *per cent.* of lime, and 75.74 sugar and water. When decomposed by carbonic acid, the sugar is evolved unaltered. (BERZELIUS.) The formula of this salt appears to be  $3\text{CaO} + \text{C}_{24}\text{H}_{21}\text{O}_{21} + 7\text{HO}$ . (PELIGOT.)

*Glucoside of baryta* was obtained by Peligot by dissolving baryta and the sugar in separate portions of pyroxylic spirit, and then mixing the solutions so as to leave slight excess of sugar: it falls in the form of a white flocculent precipitate, which must be immediately washed with the spirit, pressed, and dried in vacuo, first over lime to absorb the vapor of water, and then over sulphuric acid, which abstracts the wood-spirit. This compound is rendered slightly yellow when heated to  $212^{\circ}$ ; at a higher temperature it swells up and blackens, and its decomposition yields other products afterwards to be noticed.

*Glucoside of lead* is formed by adding a cold aqueous solution of the sugar to an ammoniacal solution of oxide of lead: the precipitate at first formed, redissolves, and then appears again when there is slight excess of sugar; it must be collected and dried at ordinary temperature, with the usual precautions to avoid absorption of carbonic acid: it may then be dehydrated by exsiccation in vacuo at  $212^{\circ}$ , by which, however, it is rendered slightly yellow. Its formula, according to Peligot, is  $6\text{PbO}, \text{C}_{24}\text{H}_{21}\text{O}_{21}$ .

*Glucoside of chloride of sodium* was first obtained by Calloud (*Journ. de Pharm.*, xi. 562,) by evaporating a mixed solution of diabetic sugar and common salt. It is easily formed by saturating a moderately-strong solution of grape sugar with the salt, and slowly evaporating; some chloride of sodium is at first deposited, and afterwards the saccharine salt forms in colorless double six-sided pyramids, hard and brilliant. They may be purified by a second solution and crystallization: they are readily soluble in water, and have a salt sweet taste; they are scarcely soluble in alcohol: they are represented by  $\text{NaCl} + \text{C}_{24}\text{H}_{21}\text{O}_{21} + 5\text{HO}$ . but when dried at  $212^{\circ}$ , they lose a part of their water of crystallization. (PELIGOT.)

The action of grape sugar upon many metallic salts is distinct from that of cane sugar, and is attended by the reduction of the oxides which they contain, either to a lower degree of oxidizement, or to the state of metal, and accordingly some of these salts are resorted to as valuable tests of the presence of grape sugar, both qualitative and quantitative; and as cane sugar is easily converted into grape sugar, by boiling it with a little sulphuric or other acid, both kinds of sugar may be thus detected, or they may be distinguished from each other. Some of the salts of copper, mercury, silver, gold and platinum are especially applicable to these purposes.

When a little cane sugar is added to a dilute solution of sulphate of



copper, and the mixture boiled, little change ensues; but with grape sugar the blue color of the liquor is presently changed to green, it then becomes yellowish or reddish-brown, and suboxide of copper or metallic copper falls: these changes are more rapid when a little alkali has been added to the solution. The best form of copper test of the presence of grape sugar is the *soda tartrate of copper* already noticed (p. 1183), obtained by dissolving recently precipitated tartrate of copper in a solution of soda or of carbonate of soda: it is immediately discolored and reduced when boiled with a trace of grape sugar; and when used quantitatively, it will be found that 15 parts of the precipitated suboxide of copper are equivalent to about 5 grains of crystallised cane sugar. A hot solution of nitrate of suboxide of mercury is immediately blackened by grape sugar, and finely divided metallic mercury falls: in the same way a boiling solution of corrosive sublimate deposits calomel, which is afterwards partially reduced: red oxide of mercury is also reduced when boiled in a saccharine solution. Solutions of nitrate of silver and of chloride of gold, when boiled with grape sugar, afford precipitates of finely divided silver and gold: when in these cases excess of carbonate of soda is present, the effect is more rapid, and in this way the chlorides of platinum and palladium are easily reduced. The advantage of soda or carbonate of soda is that it does not form insoluble precipitates with the metallic solutions generally used. An exceedingly delicate and useful test of the presence of grape sugar is the soda-chloride of platinum formed by adding excess of a solution of carbonate of soda to a moderately dilute chloride of platinum. When this solution is boiling, an atom of cane sugar dropped into it produces no effect, but, as I have already observed, it is instantly discolored and ultimately blackened by the smallest trace of grape sugar. Mr. Lewis Thompson, who first pointed out to me the value of this test, assumes 12 grains of the precipitated metallic platinum, to be the equivalent of 5 grains of ordinary cane sugar. When a little tartaric acid is added to chloride of palladium, and then excess of carbonate of soda, a liquor is obtained which is immediately blackened when boiled with grape sugar, and metallic palladium is deposited: this solution is also immediately reduced by alcohol; and in all cases where these tests are used in reference to the presence of sugar, the absence of other organic matters likely to affect their decomposition, must be carefully ensured.

**HONEY.** The substance secreted in the nectaries of flowers is collected by bees, and by them converted into honey and wax; the portion of sugar not required for nutriment is returned by the insect into the combs, in the form of a yellow syrup, the taste and smell of which differ a little, according to the flowers whence it has been derived, but which is always yellow, viscid, and very sweet. Honey contains two kinds of sugar; the one resembles that from the grape; the other is uncrystallizable, and probably identical with the analogous sugar which is found along with common sugar in cane juice; honey also contains a yellow coloring-matter, wax, gum, and sometimes manna sugar. The solid sugar is most easily obtained from the granular or crystalline honey, by the action of strong alcohol, which dissolves the other ingredients, but leaves the granular sugar. It may be whitened by dissolving it in water, filtering, boiling with charcoal, and evaporating the solution till it granulates when cold.

**MANNITE. MANNA SUGAR.** This species of sugar is most abundant in manna, but is also found in beet root, celery, asparagus, onions, and probably in many other sweet plants: it is also contained in the sap of the *larch* (and other species of *pinus*), and exudes from their bark, but it always tastes of turpentine: (*Manna Brigantina*.) It has been detected by Dr. Stenhouse in *Laminaria saccharina*, and some other fuci. (*Mem. Ch. Soc.*, II. 136.) Manna exudes from several species of *ash*, especially from the *Fraxinus ornus*, and *rotundifolia*. (In reference to the mode of collecting and preserving manna, see PEREIRA, *Mat. Med.*, p. 1320. The varieties of manna which occur in commerce, have also been described by LEUCHTWEISS, *Chem. Gaz.*, August, 1845.) The purest and finest manna of commerce is called *flake-manna*, and is imported from Sicily and Calabria; it is of a buff color, light, and translucent. It has a slight odor, and a sweet, somewhat nauseous taste. *Mannite* is obtained by boiling manna in alcohol: as the solution cools, it crystallizes: it may be purified by pressure. By very slow crystallization it furnishes delicate four-sided acicular prisms. It forms about four-fifths of the best manna; the residue is common sugar, and a peculiar yellowish extractive matter, in which the aperient quality of the manna is said to reside. Mannite may also be obtained from the fermented juice of beet-root after the viscous fermentation is over, by evaporating it to the consistency of syrup, and adding its volume of alcohol, by which mucilage is thrown down, and on evaporating the filtered alcoholic liquor, mannite is deposited, at first much colored, but becoming white by repeated solution and crystallization. Another source of mannite is the root of celery, from which it may be obtained to the amount of 6 or 8 *per cent*.

Mannite is white, or nearly so, and very soluble in water: its aqueous solution, when sufficiently concentrated, concretes. Even when much diluted, it does not ferment; so that it may in this way be separated from the other varieties of sugar; for, when mixed with them, it remains undecomposed in the ordinary process of fermentation, whilst they are converted into alcohol. Mannite is little soluble in cold alcohol, but abundantly taken up by boiling alcohol. It fuses when heated, without losing weight, and on cooling concretes into a crystalline mass: at high temperatures it affords the same products of decomposition as common sugar. Nitric acid converts it into saccharic and oxalic acid, without any trace of mucic acid. Its aqueous solution dissolves oxide of lead.

According to Favre, the formula of crystallized mannite is  $C_6H_7O_6$ , and in combining with oxide of lead it throws off two equivalents of water, the composition of *mannaide of lead* being  $2PbO + C_6H_5O_4$ . (*Ann. Ch. et Ph.*, Mai, 1844.)

**LIQUORICE SUGAR. GLYCYRRHIZINE.** When a strong infusion of liquorice root is slowly evaporated to a small bulk, and sulphuric acid added, a precipitate falls containing sugar and albumen, which is to be washed with water acidulated by sulphuric acid, then with pure water, and afterwards digested in alcohol, which leaves the albumen. A solution of carbonate of potassa is then dropped into the alcoholic solution till its acid is neutralized: it is filtered and evaporated, and the sugar remains in the form of a yellow transparent mass.

According to Vogel (*Journ. fur prakt. Chem.* and *Chem. Gaz.*, Apr. VOL. III.



1843,) a purer sugar may be obtained by carefully adding to a strong infusion of liquorice root, a solution of basic acetate of lead, washing the precipitate, diffusing it in water, and decomposing it by sulphuretted hydrogen: the mixture holds the sulphuret of lead obstinately in suspension, but after having been several times boiled, it admits of perfect filtration: the filtered solution is then evaporated cautiously to dryness, and the residue dissolved (repeatedly) in absolute alcohol: it is thus freed from bases and acids, and may be obtained in bright yellow pieces, which burn with a smoky flame without residue.

Liquorice sugar is intensely sweet, uncrystallizable, and easily soluble in alcohol and in water: it is characterized by its tendency to combine with acids, bases, and salts: its composition has been expressed by  $C_{16}H_{12}O_{12}$ . *Sulphate of glycyrrhizine* is tough, and sweet without acidity: it dissolves in boiling water, and gelatinizes on cooling: its alcoholic solution is not precipitated by water. *Acetate of glycyrrhizine* resembles the sulphate, but is more soluble, and forms a stiffer jelly. Glycyrrhizine combines with bases, and, when digested with alkaline carbonates, gradually displaces carbonic acid, and forms soluble compounds, which are not decomposed by carbonic acid. It occasions precipitates with most metallic salts. The precipitate produced by chloride of barium in aqueous solution of glycyrrhizine is a definite combination of the sugar with baryta, and when pure is perfectly soluble in hydrochloric acid. An analogous sugar has been found in the leaves of the *Abrus præcatorius*, and in the root of the *Polypodium vulgare*. (BERZELIUS.)

MUSHROOM SUGAR was discovered by Braconnot, in several species of *agaricus*, and other *fungi*, and by Schrader in *morels*: (*Helvella mitra*.) It is obtained by triturating the fungus with a little water, pressing it, and evaporating the expressed liquid nearly to dryness: the dry residue is digested in alcohol, and the solution yields crystals of the sugar on evaporation; they are square prisms, colorless when pure, slightly sweet, and less soluble than cane sugar. Concentrated sulphuric acid forms with it a red solution, from which a white coagulum separates on the addition of water. This kind of sugar is now supposed to be identical with mannite.

SUGAR OF ERGOT OF RYE. Wiggers and Chevallier detected a peculiar form of sugar in ergot, soluble in alcohol, and crystallizing in transparent prisms of a pure sweet taste, very soluble in water. It is said to differ from common sugar in not reducing acetate of copper when long boiled with a solution of that salt. Its composition is represented as  $C_{24}H_{26}O_{26}$ .

#### § IV. GUM, MUCILAGE, AND THEIR VARIETIES. PECTINE AND PECTIC ACID. MUCIC ACID AND PYROMUCIC ACID.

UNDER the term *gum* are included several modifications of a distinct proximate principle of vegetables, which are of extremely common and almost universal occurrence. To some of these the term *mucilage* is occasionally applied. They are characterised by forming a viscid, adhesive, or mucilaginous solution with water, and by insolubility in alcohol; so that the addition of alcohol to a moderately strong aqueous solution of gum occasions the separation of a white precipitate or magma. There is

another characteristic property of gum, which is its convertibility into mucic or sacclactic acid by the action of nitric acid.

GUM occurs in the form of an exudation upon the bark of trees, and collects into drops which gradually harden by exposure; it may also be discovered, more or less abundantly, in the sap and juices of almost all plants and fruits, where it is recognised by the properties we are about to describe. There are two leading modifications of gum, one of which is well represented by gum arabic, and the other by gum tragacanth: there are also many intermediate varieties, among which cherry-tree gum has been especially noticed, so that the different kinds of gum have been classed under the generic terms of *Arabine*, *Tragacanthine*, and *Cerasine*.

GUM ARABIC is the produce of various species of *acacia*: it is imported from the Levant, Barbary, Senegal, the Cape of Good Hope, and India: it occurs in rounded pieces, or *tears*, and in fragments of various sizes; and when pure is brittle, transparent or translucent, colorless or pale yellow, tasteless, inodorous, and of a specific gravity varying between 1.30 and 1.50. It does not crystallize, but when its aqueous solution is slowly evaporated, it remains in a hydrated state, and, though apparently dry, retains about 17 *per cent.* of water, which is given off by desiccation in vacuo over sulphuric acid, at 212°. Heated above 212° it becomes yellowish, and slightly sour; and when subjected to destructive distillation, yields acid water, empyreumatic oil, carbonic acid and carburetted hydrogen, and a spongy residue of charcoal, which leaves about 3 *per cent.* of ash, consisting chiefly of carbonate of lime and carbonate of potassa, with traces of silica.

Gum arabic is soluble in cold water, and more rapidly in boiling water, yielding a solution which is more or less viscid and clammy according to the proportion of gum; it slightly reddens litmus. This solution is sometimes used as a glaze or varnish, and to give a gloss and stiffness to ribands, calico, &c. When substances, in a state of minute mechanical division, are suspended in it, it prevents their subsidence; hence its employment as an ingredient of writing-ink, and of some paints. Gum is insoluble in absolute alcohol and in ether; hence alcohol occasions a white precipitate of hydrated gum, when added to its aqueous solution.

ACTION OF ACIDS ON GUM. When powdered gum arabic is triturated into a paste with *sulphuric acid*, the mixture gradually becomes brown, and if, after it has stood for 24 hours, it is diluted with water and saturated by chalk, so as to abstract the acid, the gum retained in solution is somewhat modified, and resembles that which we shall afterwards describe as produced by the action of sulphuric acid upon lignine. Heated with sulphuric acid, gum is decomposed; sulphurous acid, and traces of acetic acid, and of artificial tannin are formed, and about 30 *per cent.* of carbon deposited upon the addition of water. Boiled with *very dilute* sulphuric acid, it is gradually converted into grape sugar or glucose. *Nitric acid* decomposes gum, and, when aided by heat, nitric oxide is evolved, and from 14 to 26 *per cent.* of mucic acid deposited on cooling. Longer digestion produces malic and oxalic acid. It would appear, from Vauquelin's experiments, that when chlorine is passed through a solution of gum, a portion of citric acid is generated, but this requires verification. Powdered gum absorbs chlorine, and becomes brown and soft; it also absorbs hydro-



chloric acid, becoming brown, viscid, and evolving the gas when acted on by sulphuric acid. Iodine is apparently without action upon gum.

**ACTION OF BASES ON GUM.** The action of salifiable bases, and of certain salts, upon gum, has been inquired into by Berzelius, Pfaff, Bostock, Thomson, and several other chemists. According to Berzelius, a concentrated solution of gum is first coagulated by caustic potassa, and then gradually liquifies; alcohol throws down from the solution a compound of gum and potassa in the form of a curdy precipitate, which, when dried, is brittle and soluble in water: similar combinations may be made with the other alkalis and the alkaline earths. When recently-precipitated hydrated oxide of lead is digested in an aqueous solution of gum, a definite compound of gum and oxide of lead is formed: the same compound is obtained by adding subnitrate or subacetate of lead to a solution of gum, or by adding ammonia, not in excess, to a mixed solution of gum and nitrate of lead; it is white and insoluble, and when carefully dried consists of 61·75 gum, and 33·25 oxide of lead. A solution of *gum arabic* is precipitated by silicate of potassa: it is coagulated by a solution of borax, and the coagulum is soluble in free acid: in this respect gum resembles starch. When persulphate of iron is dropped into solution of gum arabic, a yellow gelatinous precipitate falls, soluble in free acid and in caustic potassa, but only partially soluble in boiling water: 1 part of gum in 100 of water gives a yellow precipitate after 24 hours. When concentrated solutions of gum and of perchloride of iron are mixed, a brown transparent jelly is formed which is difficultly soluble in water: if the solution of perchloride of iron be so dilute as to be almost colorless, the addition of gum renders it yellow, and after some hours a white precipitate insoluble in nitric acid is deposited. (DUMAS.) This action upon persalts of iron is peculiar to gum arabic. Protonitrate of mercury also affords a precipitate with gum. (BERZELIUS.) Oxalate of ammonia gives a precipitate of oxalate of lime in a solution of gum arabic, but the nature of the salt of lime originally present in the gum has not been satisfactorily ascertained; Thomson states it to be a bimalate. *Gum senegal* is said to resemble gum arabic, and to be derived from certain species of *acacia*.

**GUM TRAGACANTH** is the produce of certain species of *Astragalus*: according to Olivier the greater part of that which comes to Europe is obtained in Asia Minor, Armenia, and Northern Persia, from the *Astragalus verus*, and is imported from Smyrna: it is often called in the shops *gum dragon*; the inferior varieties are used as mucilage, chiefly by shoemakers; it is employed in medicine as a demulcent, and as a vehicle for heavy insoluble powders. It is generally in the form of white or yellowish semitransparent flakes, or curled, crinkled, and vermicular pieces, and so tough as not to admit of being powdered till dried at 212°, when it loses about 10 *per cent.* of water, and becomes brittle. It does not dissolve like gum arabic, but when steeped in water swells into a bulky mucilaginous mass, which, when boiled with water, gradually acquires the appearance of a solution of ordinary gum, in consequence, probably, of its transmutation into arabine. According to Guérin Varry, 100 parts of tragacanth yield 53 of *arabine*, or gum analogous to gum arabic, and 33 of *tragacanthine* or *Bassorine*, a mucilaginous substance, described by Vauquelin as forming the bulk of gum Bassora,

(*Ann. du Museum*, xvi. 167), the remainder being water and oxalate of lime.

CHERRY-TREE GUM and that of *peach* and *apricot* trees, and other species of *Prunus*, resembles inferior gum arabic in appearance, but is only partially soluble in cold water; it neither gelatinises with persulphate of iron, nor does it precipitate silicate of potassa or protonitrate of mercury, but it forms a gelatinous precipitate with chloride of tin.

MUCILAGE is a term applied to a substance which water, heated to 160° or 180°, extracts from certain seeds or roots when they are infused in it, and then subjected to pressure in a linen strainer: when the liquor is evaporated the residue resembles gum. When bruised *linseed* is thus treated, it yields a mucilaginous solution, which is precipitated by acetate and subacetate of lead, by chloride of tin, and by alcohol; it leaves a gumlike substance on evaporation, which swells up, and dissolves in water, and the properties of which closely resemble those of gum arabic. *Quince seed* boiled in water furnishes a similar mucilaginous liquor. "One part of quince seed forms with 40 parts of water a thick mucilage, which produces with the following salts, gelatinous coagula or precipitates; acetate and diacetate of lead, protochloride of tin, nitrate of mercury, and sesquichloride of iron. Rectified spirit produces at first scarcely any effect, but after some time partial coagulation ensues. Oil of vitriol communicates a pinkish tint, and causes the separation of a frothy coagulum, which floats on the mixture. Silicate of potassa, infusion of galls, and oxalate of ammonia, produce no change in this mucilage. It appears to be a peculiar substance, hence I propose to call it *Cydonine*. It is distinguished from arabine by the effect of alcohol, sulphuric acid, silicate of potassa, and oxalate of ammonia; from bassorine and cerasine by its solubility both in hot and cold water; from tragacanthine by the effect of sulphate of iron, oxalate of ammonia, and alcohol; from carrageenine, by the effect of silicate of potassa, and acetate of lead." (PEREIRA. *Mat. Med.*, ii. 1555.) This mucilage appears to reside in the husk or outer coat of the quince seed: it is used by ladies, under the name of *fixature*, to retain the hair in curl. *Calenduline* is a mucilage obtained from the petals of the *Calendula officinalis*, or common marigold. *Carrageenine* is the gelatinous principle of the *Chondrus crispus*, or *Carrageen moss*; it is soluble in boiling water, and its solution forms a precipitate with diacetate of lead and with silicate of potassa, and if sufficiently concentrated gelatinizes on cooling. It is distinguished from ordinary gum by its aqueous solution not producing a precipitate on the addition of alcohol; from starch, by its not assuming a blue color with iodine; from animal jelly, by tincture of galls producing no precipitate; from pectine, by acetate of lead not throwing down anything, as well as by no mucic acid being formed by the action of nitric acid. (PEREIRA, *Mat. Med.*, ii. 874.)

SALEP is the root of several species of indigenous *orchis*; when cleansed and boiled for a short time in water, it yields a disagreeable extract; by more prolonged boiling it almost entirely dissolves into a transparent mucilage.

SARCOCOLLINE is the concrete juice of the *Penaea sarcacolla*, a plant growing in the northern parts of Africa: it somewhat resembles gum arabic in appearance, but it dissolves in proof spirit, and its aqueous



solution is precipitated by infusion of galls. Several other modifications of gum and mucilage have been described, many of which are found blended with resins and volatile oils in the substances termed *gum resins*.

The ultimate elements of gum are those of a hydrate of carbon, and its atomic composition may be represented by the formula  $C_{12}H_{11}O_{11}$ , or  $C_{24}H_{22}O_{22}$ : under the first formula its equivalent will be 171, and it will be represented by  $C_{12},11HO$ ; or

|               |    |     |     | Gay Lussac<br>and Thenard. |         | Berzelius. | Prout. | Göbel. |         |     |       |     |       |
|---------------|----|-----|-----|----------------------------|---------|------------|--------|--------|---------|-----|-------|-----|-------|
| Carbon .....  | 12 | ... | 72  | ...                        | 42·106  | ...        | 42·23  | ...    | 42·682  | ... | 41·4  | ... | 42·2  |
| Hydrogen..... | 11 | ... | 11  | ...                        | 6·432   | ...        | 6·93   | ...    | 6·374   | ... | 6·5   | ... | 6·6   |
| Oxygen.....   | 11 | ... | 88  | ...                        | 51·462  | ...        | 50·84  | ...    | 50·944  | ... | 52·1  | ... | 51·2  |
| <hr/>         |    |     |     |                            |         |            |        |        |         |     |       |     |       |
| Anhydrous gum | 1  |     | 171 |                            | 100·000 |            | 100·00 |        | 100·000 |     | 100·0 |     | 100·0 |

According to Berzelius, the compound of gum with oxide of lead, *gummide of lead*, contains 38·25 *per cent.* of oxide, so that it would be  $PbO, C_{12}H_{11}O_{11}$ , consisting of

|                      |   |     |     |     |        |            |
|----------------------|---|-----|-----|-----|--------|------------|
|                      |   |     |     |     |        | Berzelius. |
| Oxide of lead .....  | 1 | ... | 112 | ... | 39·58  | ... 38·25  |
| Gum.....             | 1 | ... | 171 | ... | 60·42  | ... 61·75  |
| <hr/>                |   |     |     |     |        |            |
| Gummide of lead..... | 1 |     | 283 |     | 100·00 | 100·00     |

Mulder has lately examined the purified mucilages of tragacanth, linseed, and quince seed, and adopts for them the formula  $C_{22}H_{19}O_{19}$ ; but the analyses upon which this conclusion is founded are by no means satisfactory. (*Journ. für prakt. Chem.*, xxxvii. 334.)

**PECTINE. PECTIC ACID.** Under these terms (from *πηκτις*, *coagulum*), Braconnot has described the *jelly* of fruits, a substance which had generally been regarded as a compound of gum and vegetable acid: it had been distinguished from animal jelly as not containing nitrogen. It is obtained from many fruits, by carefully expressing their juice and evaporating it more or less, at a temperature not exceeding  $212^{\circ}$ . It may be obtained by the addition of alcohol to the recently-expressed juice of ripe currants or gooseberries: in the course of a few hours a gelatinous substance separates, which must be washed with weak alcohol and dried: it then resembles isinglass in appearance, and, when digested in cold water, swells into a soft pulp somewhat like starch; it is not blued by iodine. It may also be procured from the rasped roots of carrots and turnips. Deposited from a mixture of one-fourth of the juice of cherries and three-fourths of the juice of gooseberries, and washed carefully, first with dilute alcohol, and then with cold distilled water, it is pure, with the exception of a little coloring-matter. When heated with a small quantity of potassa, or soda, or of their carbonates, it is converted into what has been termed *Pectic acid*. This acid is easily obtained by the action of alkalis on the ligneous tissue of some vegetables: it combines with bases, and may be again separated from them by other acids. (BRACONNOT, *Ann. Ch. et Ph.*, xxviii. and xxx.) The *alkaline pectates* are soluble, but the *pectate of lime* is insoluble.

To obtain *pectic acid* from carrots or turnips, they are rasped into pulp, which is pressed so as to extract its juice; the residue is then washed in cold water till all soluble matters are removed, and blended

with 6 or 8 times its weight of water, to which one-tenth of its weight of carbonate of soda, or one-fiftieth of caustic potassa, is added; this mixture is boiled for half an hour, and filtered whilst hot: the liquor holds pectate of potassa or of soda in solution, and might at once be decomposed by an acid, but in that case the pectic acid is difficultly washed, so that it is better to decompose the alkaline pectate by the addition of a very dilute solution of chloride of calcium, which throws down an insoluble pectate of lime; this may be well washed, and then boiled in water acidulated by hydrochloric acid, by which the lime is abstracted and the pectic acid separated; it should be edulcorated with cold water.

When thus purified, pectic acid forms a tasteless jelly; it has been much recommended in France as a part of the diet of invalids, and it is said to be an antidote in cases of poisoning by certain metallic salts with the oxides of which it forms insoluble compounds (*Ann. Ch. et Ph.*, xxx. 96.) It gives the gelatinous character to certain soups prepared from the roots which yield it. To produce an agreeable jelly, Braconnot recommends 1 part of the gelatinous pectic acid to be mixed with 3 of distilled water, adding gradually an extremely dilute solution of soda so as to render the liquor slightly alkaline; it is then heated, and some sugar is added, a portion of which has been flavored by rubbing it upon the peel of a lemon; a very slight excess of dilute hydrochloric acid is then added, and on stirring the mixture it soon gelatinizes; the flavor of rose, vanilla, cinnamon, cloves, &c., may be similarly imparted; and if required, noyau, maraschino, and other alcoholic jellies may in the same way be prepared: these preparations are liable to become mouldy when kept, but they do not become sour.

The ultimate composition of pectic acid has not been satisfactorily determined, nor has its equivalent been ascertained. Regnault represents it as  $C_{12}H_7O_{10} + HO$ ; Mulder as  $C_{12}H_8O_{10}$ ; and Chodnew adopts the formula  $C_{28}H_{18}O_{24} + 2HO$ : in all these formulæ there is excess of oxygen over hydrogen, and they agree in the absence of nitrogen; but whether pectic acid should be regarded as monobasic or bibasic, is not as yet evident.

**PECTATES.** The *pectates of ammonia, potassa, and soda*, are gelatinous compounds, soluble in water: their aqueous solutions give precipitates of *subpectates*, on the addition of potassa or soda, but not with ammonia. The neutral pectate of ammonia becomes acid on drying, but resumes its gelatinous state in water. Those bases, the carbonates of which are insoluble, form insoluble combinations with pectic acid; they are best obtained by double decomposition with neutral pectate of ammonia. Some of these pectates are a little soluble in solutions of the alkaline pectates, such as those of antimony, mercury, and silver; but the pectates of zinc, lead, and copper, are insoluble. The neutral pectate of potassa contains 15 *per cent.* of base; when dried it forms a tasteless gumlike substance, slowly soluble in cold water; at a heat approaching to dull redness, it is converted into ulmate of potassa, and at a higher heat it leaves a bulky mixture of charcoal and carbonate of potassa. *Pectate of copper* falls in the form of a green gelatinous hydrate; it is not acted on by hot or cold water, or dilute acetic acid; dilute nitric acid abstracts its base, and sets the pectic acid free; the other stronger acids



produce the same effect. Caustic potassa converts it into a *subpectate* by combining with part of its acid. (BRACONNOT, *Ann. Ch. et Ph.*, xxviii., xxx., XLvii., and L. DUMAS, *Chim. app. aux Arts.*) Braconnot has separated a substance from parsley (*Apium petroselinum*), which he terms *Apiine*, and which he describes as having many of the properties of pectine. (*Ann. Ch. et Ph.*, October, 1843.)

**MUCIC ACID. SACLACTIC ACID.** This acid is produced by the action of nitric acid upon the principal varieties of *gum*, and upon *lactine*, or *sugar of milk*. It was discovered by Scheele. (*Opusc.*, ii. 3.) It is obtained by heating in a sufficiently capacious retort, about 3 parts of pulverised gum arabic, and 5 of nitric acid diluted with half its weight of water; carbonic acid and nitrous gas are evolved, and when the effervescence has nearly ceased, the mixture is allowed to cool: it then deposits a white sediment, which is mucic acid mixed with a little oxalate of lime. 1 part of *sugar of milk* may be substituted for the gum, and exactly the same product is obtained. It may be purified as follows: add ammonia, in slight excess, to the impure acid, and afterwards as much boiling distilled water as will dissolve the salt formed. Filter the solution while boiling-hot, and then evaporate it very slowly, nearly to dryness. The *mucate of ammonia* will be separated in the form of crystals, which are to be washed with cold distilled water till they become quite white and pure. They are now to be again dissolved in distilled water, and the boiling saturated solution permitted to drop from a filter into cold diluted nitric acid. This latter, of course, decomposes the mucate, and precipitates the acid in a state of purity. (PROUT. *Phil. Trans.*, 1827.)

Mucic acid is sparingly soluble in water, requiring 60 parts, at  $212^{\circ}$ , and is deposited, as the solution cools, in the form of a white gritty powder, of a slightly acid taste. It is insoluble in alcohol. It is decomposed when boiled with concentrated nitric acid, and a black brilliant carbonaceous matter is formed. When heated to about  $400^{\circ}$ , with caustic potassa, hydrogen is disengaged, and acetate and oxalate of potassa are formed. A saturated aqueous solution of this acid occasions precipitates in lime, baryta, and strontia water, which are redissolved by excess of the acid.

Mucic acid is bibasic, being represented by the formula  $C_{12}H_8O_{14} + 2HO$ ; or  $\bar{M} + 2HO$ : as it exists, therefore, in the *anhydrous mucates*, its components are

|                      |    |     |     |     |        |
|----------------------|----|-----|-----|-----|--------|
| Carbon .....         | 12 | ... | 72  | ... | 37.50  |
| Hydrogen .....       | 8  | ... | 8   | ... | 4.17   |
| Oxygen .....         | 14 | ... | 112 | ... | 58.33  |
| <hr/>                |    |     |     |     |        |
| Anhydrous mucic acid | 1  |     | 192 |     | 100.00 |

And in the ordinary hydrated (or crystallized) acid, there are two added atoms of water, its ultimate elements being

| Gay Lussac               |    |      |     |      |                        |      |        |            |        |      |        |      |         |
|--------------------------|----|------|-----|------|------------------------|------|--------|------------|--------|------|--------|------|---------|
|                          |    |      |     |      | Malaguti. and Thenard. |      | Prout. | Berzelius. |        |      |        |      |         |
| Carbon .....             | 12 | .... | 72  | .... | 34.28                  | .... | 34.73  | ....       | 33.69  | .... | 33.33  | .... | 33.430  |
| Hydrogen....             | 10 | ..   | 10  | .... | 4.76                   | .... | 4.73   | ....       | 3.62   | .... | 4.94   | .... | 5.105   |
| Oxygen.....              | 16 | ...  | 128 | .... | 60.96                  | .... | 60.54  | ....       | 62.69  | .... | 61.73  | .... | 61.465  |
| <hr/>                    |    |      |     |      |                        |      |        |            |        |      |        |      |         |
| Hydrated<br>mucic acid } |    |      | 210 |      | 100.00                 |      | 100.60 |            | 100.00 |      | 100.00 |      | 100.000 |

MUCATES. SACLACTATES. There are two series of these salts, namely, one with 2 atoms of fixed base, and one with 1 atom of fixed base and 1 atom of constitutional water; their formulæ therefore are,  $2\text{MO} + \text{C}_{12}\text{H}_8\text{O}_{14}$ , and  $\text{MO},\text{HO} + \text{C}_{12}\text{H}_8\text{O}_{14}$ .

*Mucate of ammonia.*  $2[\text{NH}_4\text{O}] + \text{C}_{12}\text{H}_8\text{O}_{14}$ ; or  $2[\text{NH}_4\text{O}] \overline{\text{M}}$ , is prepared by supersaturating a hot solution of mucic acid with carbonate of ammonia; it crystallizes in flattened parallelopipeds, which are not decomposed by being heated to  $230^\circ$ . (MALAGUTI.)

With *potassa* and with *soda* mucic acid forms neutral and acid salts; in the former, 2 atoms of base are combined with 1 atom of acid; in the latter, 1 atom of base, 1 of water, and 1 of acid, are the constituents: these salts have as yet been but imperfectly examined. *Mucate of lead*,  $2\text{PbO}, \overline{\text{M}}, + 2\text{HO}$ , falls in the form of a white powder, on adding an aqueous solution of mucic acid or of a soluble mucate, to any neutral solution of a salt of lead; its components are

|                     |   |     |       |     |        | Trommsdorff. | Berzelius. |
|---------------------|---|-----|-------|-----|--------|--------------|------------|
| Oxide of lead ....  | 2 | ... | 224   | ... | 51.61  | ... 51.5     | ... 51.66  |
| Mucic acid.....     | 1 | ... | 192   | ... | 44.24  | ... } 48.5   | ... 48.34  |
| Water .....         | 2 | ... | 18    | ... | 4.15   |              |            |
| <hr/>               |   |     | <hr/> |     | <hr/>  |              | <hr/>      |
| Mucate of lead .... | 1 |     | 434   |     | 100.00 | 100.0        | 100.00     |

*Mucate of silver* also includes 2 atoms of oxide of silver.

PARAMUCIC ACID. MODIFIED MUCIC ACID. Laugier has observed that when a saturated aqueous solution of mucic acid is boiled and evaporated, it leaves a slightly-colored residue, the acid properties of which exceed those of the ordinary acid; yet, according to Malaguti, these acids are similarly constituted. The acid thus modified, is more soluble in water; and it is soluble in alcohol, and may be obtained from this solution in square tabular crystals. It is soluble in 73 of cold, and 17 of boiling water, and when its hot saturated aqueous solution cools, it deposits crystals having the properties of the ordinary acid. Its salts are generally more soluble than the common mucates; but when a hot saturated solution of the modified acid is neutralized by ammonia, a difficultly-soluble ammoniacal salt falls; whereas with the common acid, crystals are a long time in forming. From the analysis of modified mucate of silver, Malaguti is inclined to believe that the difference between this and the common acid may depend upon the presence of an additional atom of water in the former. (*Ann. de Chimie*, Lxii. 81; *Journ. de Pharm.*, xxi. 640.)

PYROMUCIC ACID.  $\text{C}_{10}\text{H}_8\text{O}_5,\text{HO}$ . When mucic acid is subjected to destructive distillation, it yields carbonic acid and water, and about one-fifteenth of its weight of *pyromucic acid*, part of which sublimes, and part dissolves in the distilled liquid. To purify it, the whole is dissolved in water, and filtered through animal charcoal, evaporated, and crystallized, or again sublimed. This acid is permanent in the air, inodorous, very sour, fusible at  $270^\circ$ , and rises in vapor at a few degrees above that point, condensing in drops which concrete in fine acicular crystals, soluble in 26 parts of cold, and in less of boiling water, and more soluble in alcohol. (HOUTON LABILLARDIÈRE,



*Ann. Ch. et Ph.*, ix. 365.) It consists, in its anhydrous or combined state, of

|                      | Boussingault. |      |     |      |       |            |
|----------------------|---------------|------|-----|------|-------|------------|
| Carbon .....         | 10            | .... | 60  | .... | 58.3  | .... 58.74 |
| Hydrogen .....       | 3             | .... | 3   | .... | 2.9   | .... 2.88  |
| Oxygen .....         | 5             | .... | 40  | .... | 38.8  | .... 38.38 |
| <hr/>                |               |      |     |      |       |            |
| Pyromucic acid ..... | 1             |      | 103 |      | 100.0 | 100.00     |

The crystallized acid appears to include an atom of water; so that its ultimate elements are,  $C_{10}H_4O_6$ , or  $C_{10}H_3O_5 + HO$ ; and in its formation, 1 atom of hydrated mucic acid is resolved into 1 atom of hydrated pyromucic acid, 2 of carbonic acid, and 6 of water:  $C_{12}H_{10}O_{16} = C_{10}H_4O_6 + 2CO_2 + 6HO$ . It is a monobasic acid, the water of the hydrated acid being replaced in the salts, by 1 atom of base.

*Pyromucates.* The greater number of these salts are soluble in water; the pyromucates of potassa and soda are deliquescent, and soluble in alcohol: the pyromucates of lime, baryta, and strontia, are rather more soluble in hot than in cold water, and insoluble in alcohol. The pyromucates of oxide of lead, of oxide of silver, of protoxide of iron, and of protoxide of manganese, are soluble, but that of peroxide of iron is insoluble, and of a yellow color: the pyromucate of protoxide of mercury is also nearly insoluble.

## § V. LIGNINE.

LIGNINE forms what may be termed the skeleton of plants, being, as it were, the fundamental material of their structure, and of the fabrics in which their various secretions and proximate principles are contained. In order to obtain it, woody fibre in the form of fine sawdust may be successively boiled in alcohol, water, weak solution of potassa, dilute hydrochloric acid, and ultimately again in repeated portions of distilled water; and when everything soluble is thus abstracted, the residue, carefully dried at  $212^\circ$ , may be regarded as pure lignine. In other cases, pith, or other attenuated forms of woody fibre may be operated on, and after having been rasped, and washed, first in cold and then in hot water, digested in a weak solution of potassa, and then subjected to the action of chlorine, and a second time to weak potassa, and lastly to acetic acid and repeated washing, they afford a very pure form of lignine.

There are a number of other forms in which lignine presents itself, and often in a state approaching to purity, as in linen, cotton, paper, &c. It constitutes the basis of all the varieties of wood, varying in texture from the delicate and friable pith, to the hard shells of seeds, and the more dense and indurated vegetable ivory, or perisperm of the seed of the *phytelephas*. The cleansed and bleached fibre of hemp or flax, and linen, or cotton, are good forms of lignine for many purposes of experiment, for in the processes of steeping, washing, bleaching, and so forth, they have mostly been deprived of all soluble and foreign matters.

Pure lignine is tasteless, white, and insoluble in water, alcohol, ether, and the oils; its sp. gr. is about 1.5.

When wood is thoroughly dried at a temperature of about  $220^\circ$  it shrinks and splits, or if in powder loses variably in weight, according

to its degree of humidity; and it again absorbs moisture when exposed to the air. When wood is carefully baked, so as to become of a pale-brown color, it yields a brown infusion with water, which, when carefully prepared, tastes and smells like *toast and water*: and indeed, lignine has been represented as convertible into a palatable and nutritious bread. Something of this kind is said to be used by the peasantry of Norway and Sweden; and the following directions are given for the purpose by Professor Autenrieth of Tübingen; he employed *beech* and similar woods, destitute of turpentine. "In the first place, everything that was soluble in water was removed by frequent maceration and boiling. The wood was then reduced to a minute state of division, that is to say, not merely into fine fibres, but actual powder; and after being repeatedly subjected to the heat of an oven, was ground in the usual manner of corn. Wood thus prepared, according to the author, acquires the smell and taste of corn flour. It is, however, never quite white, but always of a yellowish color. It also agrees with corn flour in this respect, that it does not ferment without the addition of leaven, and in this case sour leaven of corn flour is found to answer best. With this it makes a perfectly uniform and spongy bread; and when it is thoroughly baked, and has much crust, it has a much better taste of bread than what in time of scarcity is prepared from the bran and husks of corn. Wood flour also, boiled in water, forms a thick, tough, trembling jelly, like that of wheat starch, and which is very nutritious." (PROUT, *Phil. Trans.*, 1827.)

When wood is burned in the air, it affords large quantities of inflammable gases which by producing flame render it a valuable fuel. If decomposed under the influence of inadequate access of air, it leaves common charcoal, the relative proportions of which, as afforded by the different kinds of wood, have already been noticed (p. 444). Subjected to destructive distillation in close vessels, *water*, *empyreumatic oil* and *tar*, *pyroxylic spirit*, and *acetic acid*, together with gaseous compounds of carbon and oxygen, and carbon and hydrogen, are the results. These, and the various products into which they are resolvable, will be afterwards noticed.

Concentrated sulphuric acid converts wood in the first instance into gum or dextrine, and this may afterwards be changed into grape sugar. Thus, if about 100 parts of cotton, or shreds of linen, be gradually moistened with about 140 parts of concentrated sulphuric acid, so as to avoid evolution of heat and charring, they soon admit of being triturated into a mucilaginous magma, which is soluble in water; this solution, saturated with chalk and strained, yields a liquor from which alcohol throws down a gummy precipitate, and if this be washed with alcohol, redissolved in acidulated water, and boiled for several hours, it gradually passes into grape sugar. So that it might be inferred from these results, that lignine is convertible by the agency of cold sulphuric acid, into amidine, and dextrine, and afterwards into glucose. The evidence of the formation of starchy matter or amidine in this case is not very distinct; but if on the first action of the sulphuric acid on the cotton or linen, an aqueous solution of iodine be added, a deep blue tint is often obtained. According to Schleiden, this apparent formation of starch is best effected by wetting clean cotton wool with water, squeezing it dry, and then spreading it in a flat dish and moistening it with a mixture of



three parts of sulphuric acid, and one of water; after about half a minute, add an aqueous solution of iodine, and the blue iodide of starch will appear. (BRACONNOT, *Ann. Ch. et Ph.*, xii. 172; SCHLEIDEN, *Poggend.*, xliii. 396.)

During this action of sulphuric acid upon wood, Braconnot also observed the formation of a peculiar compound which has been termed *sulpholignic*, or *lignosulphuric acid*. When sawdust or linen rags are mixed as in the above process, with sulphuric acid, so as to form a homogeneous paste or magma, and water added, the sulpholignic acid is held, with other matters, in solution, and may be separated as follows: carbonate of baryta or carbonate of lead is added to the solution, it is filtered, and the baryta is then precipitated by dilute sulphuric acid, or the lead by sulphuretted hydrogen: the liquor is again filtered, evaporated by a gentle heat to the consistency of syrup, and mixed with alcohol, which precipitates dextrine, but dissolves the sugar as well as the free acid: after the careful evaporation of the alcohol at a low temperature, the residue is agitated with ether, which dissolves the acid and leaves the sugar: on allowing the ether to evaporate, the sulpholignic acid remains.

This acid is colorless and intensely sour; it is deliquescent and not crystallizable: when slightly heated it becomes brown, and blackens at  $212^{\circ}$ , depositing a carbonaceous matter and evolving sulphuric acid, and at a higher temperature sulphurous acid. It forms soluble salts with all the bases, producing no precipitate, either in solution of chloride of barium or of subacetate of lead. The sulpholignates of baryta and of lead are not crystallizable, and like the greater number of the other sulpholignates they are deliquescent and insoluble in alcohol. The sulpholignates of the alkalis give out sulphurous acid when gently heated, and leave a neutral sulphate, mixed with carbon. (BRACONNOT.)

*Sulpholignate of lead* dried below  $212^{\circ}$  is white and insoluble in alcohol and in ether: above  $212^{\circ}$  it becomes yellow, and evolves sulphoacetic acid and carbonic oxide. When a current of chlorine is passed through a solution of sulpholignate of lead, it is not rendered turbid, but becomes strongly acid from the formation of hydrochloric acid; a gummy compound is then produced, which, when heated, evolves chlorine, and which has the flavor of common salt. The carbonic acid of the atmosphere decomposes the sulpholignates, especially that of baryta, forming a carbonate and setting sulpholignic acid free. When nitrate of baryta or subacetate of lead are added to a solution of sulpholignic acid, sulphate of baryta or of lead are thrown down, and dextrine remains in solution. The composition of the sulpholignic acid, deduced from the analysis of the salt of lead, is represented as  $C_{36}H_{18}O_{18}, 2SO_3$ , upon the assumption that that salt includes 2 atoms of water; its formula being  $C_{36}H_{18}O_{18}, 2SO_3, PbO + 2HO$ : the salts of baryta and of lime are also represented as containing 2 atoms of water. (BLONDEAU DE CAROLLES. LIEBIG, *Chim. Organ.*, iii. 48.)

If a mixture of sawdust and sulphuric acid be heated, sulphurous acid, acetic acid, and formic acid are evolved, and a black magma remains, which, washed with water, leaves a carbonaceous residue amounting to about 43 per cent. of the wood employed.

Cold concentrated nitric acid converts lignine into *xyloidine* having

nearly the same characters as that obtained from starch; it is thrown down on the addition of water to the mixture. Xyloidine may also be formed by dipping a sheet of white paper or a piece of linen for a few minutes into nitric acid of the sp. gr. 1.48, and then into water: when dry the paper assumes somewhat of the appearance of parchment, and acquires greatly increased combustibility. When cotton-wool is similarly steeped in the strongest nitric acid, and then washed and dried, it forms a very inflammable compound: if it be steeped for some minutes in a mixture of equal parts of oil of vitriol and of nitric acid of 1.45 sp. gr., and then carefully washed and dried, it becomes explosively inflammable, and when kindled by a spark, it flashes off like gunpowder, leaving scarcely any residue: this has been called Schönbein's *gun-cotton*: it is probably either a *peroxide*, or a *nitrate of lignine*, but its ultimate composition has not been determined. Similar compounds may be obtained with tow and flax, and even with purified sawdust. The analyses of *xyloidine* by Pelouze and by Ballot, have been already quoted, (p. 1167.) Aided by heat the protracted action of nitric acid on lignine yields oxalic acid.

When lignine is boiled with hydrochloric acid, the acid becomes red and then brown, and the lignine gradually blackens but does not dissolve: when dried, it still burns with flame, showing that it has not been carbonized.

When lignine is added to fused caustic potassa, or when it is heated with a strong aqueous solution of potassa, oxalate and acetate of potassa are formed, and acids throw down a modified lignine from the alkaline liquor, which is said to be blued by iodine.

**ULTIMATE COMPOSITION OF LIGNINE.** With regard to the ultimate elements of lignine, Gay Lussac and Thenard first rendered it probable that the hydrogen and oxygen in this principle exist in it in the proportions in which they form water. The variety in which lignine occurs in different woods is so great as to render a separate examination of each of them impossible; Dr. Prout, therefore, selected *two* for the purpose of analysis, viz., the wood of the *Box* and of the *Willow*, which appeared to present the greatest contrast; the one being amongst the densest, the other the lightest of the woods. These were both treated exactly in the same manner; that is to say, they were first reduced to the form of a coarse powder by rasping, then well pulverized in a Wedgwood mortar, and afterwards sifted. Being by these means reduced to the form of impalpable powders, they were boiled in repeated portions of distilled water, till that fluid came off unchanged. After this they were similarly treated with alcohol, and finally again with distilled water. They were now exposed to the atmosphere, when in a dry and favorable state; and when they ceased to lose weight were submitted to analysis, and found to yield

|              | Box.  |      | Willow. |
|--------------|-------|------|---------|
| Carbon ..... | 42.7  | .... | 42.6    |
| Water.....   | 57.3  | .... | 57.4    |
|              | <hr/> |      | <hr/>   |
|              | 100.0 |      | 100.0   |

A known weight of each was then exposed for twenty-four hours to a temperature of 212°, and afterwards for six hours longer (by means of an oil-bath) to a temperature between 300° and 350°; and at the end of this



time the box had lost 14·6 and the willow 14·4 *per cent*. Analyzed in this state of desiccation, they were found to consist of

|              | Box.  |      | Willow. |
|--------------|-------|------|---------|
| Carbon ..... | 50·0  | .... | 49 8    |
| Water.....   | 50·0  | .... | 50·2    |
|              | <hr/> |      | <hr/>   |
|              | 100·0 |      | 100·0   |

showing that the loss of weight arose from the escape of water. These latter results nearly agree with those of Gay Lussac and Thenard, as obtained from the analyses of the prepared lignine of beech and oak, which afforded

|             | Beech. |       | Oak.   |
|-------------|--------|-------|--------|
| Carbon..... | 51·45  | ..... | 52·53  |
| Water ..... | 48·55  | ..... | 47·47  |
|             | <hr/>  |       | <hr/>  |
|             | 100·00 |       | 100·00 |

It is thus shown that lignine, like the preceding substances, may be represented as constituted of carbon and water\*, but we have no unobjectionable data from which the atomic equivalent of lignine can be inferred. Liebig assumes the formula  $C_{36}H_{22}O_{22}$  as representing the ultimate constitution of woody fibre, deducing it from Gay Lussac and Thenard's analysis of the lignine of oak; but if we deduce the formula from Prout's analysis of the lignine of box, it becomes  $C_{36}H_{24}O_{24}$ : the *per centage* relations of these formulæ are as follows:

|              |       |      |       |      | Prout. |      |       |      |       | Gay Lussac<br>and Thenard. |
|--------------|-------|------|-------|------|--------|------|-------|------|-------|----------------------------|
| Carbon ..... | 36    | .... | 216   | .... | 50·00  | .... | 36    | .... | 216   | .... 52·17                 |
| Hydrogen.... | 24    | .... | 24    | .... | 5·56   | .... | 22    | .... | 22    | .... 5·31                  |
| Oxygen.....  | 24    | .... | 192   | .... | 44·44  | .... | 22    | .... | 176   | .... 42·52                 |
|              | <hr/> |      | <hr/> |      | <hr/>  |      | <hr/> |      | <hr/> |                            |
| Lignine..... | 1     |      | 432   |      | 100·00 |      | 1     |      | 414   | 100·00                     |

Woody fibre may be combined with several metallic oxides and saline substances, and these combinations in reference to linen and especially to cotton, have highly important applications in the arts of dyeing and calico-printing; they will be again adverted to under the head of *coloring*

\* A substance apparently isomeric with starch or amidine, and which has been termed *cellulose*, is stated by Payen to constitute the cells and vessels of plants; but the distinction between cellulose and starch on the one hand, and lignine on the other, is not very intelligible. "The lignine of wood consists, according to M. Payen, of two organic principles which he has succeeded in separating; one is the primitive tissue composing the vessels of the wood, which is isomeric with starch,  $C_{12}H_{10}O_{10}$ , and is named by him *cellulose*; the other fills the cells, and constitutes the true ligneous matter." (GRAHAM.) "Recent researches have shown that wood is composed of two parts: 1, *cellulose*, which forms the parietes of the vegetable cells; and 2, *lignine*, which fills those cells and forms an incrustation on their walls: the latter dis-

solves in strong nitric acid; the former is left undissolved: again, oil of vitriol dissolves cellulose without blackening, and appears to convert it into dextrine, with which it agrees in composition; while lignine, separated from cellulose, is said to contain  $C_{35}H_{24}O_{20}$ ." (GREGORY.)

The substance which I have designated as *lignine*, and the characters of which I have given in the text, is sufficiently distinguished by the non-action of solvents, as evinced in the mode of obtaining it, and by its other chemical habitudes, as well as by its ultimate composition, from *starch*, although there can be no doubt of its convertibility into gum or dextrine, and sugar, and consequently, probably also in the first instance, into a substance having certain properties of amidine.

*matters.* We may here notice a few cases of this kind which bear upon the preservation of wood and timber, from dry rot, and other causes of decay. The powerful influence thus exerted in preventing organic decomposition and putrefaction, by *corrosive sublimate*, has already been mentioned (p. 979). That salt has been used for the purpose of impregnating timber, which, when so prepared, has been found to resist dry rot and other destructive agents, and to be durable under a variety of circumstances, in which ordinary and unprepared wood is liable to perish. Wood imbued with solutions of certain salts of iron, zinc, and copper, has also been found to be similarly protected, and for this purpose the *sulphate* and *pyrolignite* of iron, *sulphate* of copper, and *chloride* of zinc (see p. 765) have been most successfully employed. These substances appear to act in two ways: namely, either by combining with certain azotised principles existing in the wood, which are not only themselves prone to decomposition, but appear to act as ferments, and in that way to promote the destruction of the wood; or they form new and comparatively durable compounds with the wood itself: so that wood which has been steeped in a solution of a salt of iron, copper, or zinc, retains the oxides of those metals in permanent combination, and in that state resists chemical change, fungous vegetation, and the attacks of insects. The effect of any of the soluble salts of iron in permanently staining linen, or producing what is called an *iron mould*, is well known; and the impossibility of removing it by washing, boiling, or other ordinary agents, shows the powerful attraction subsisting between the linen or cotton fibre, or *lignine*, and the metallic oxide. In the same way, canvas steeped in a dilute solution of chloride of zinc is found permanently to retain oxide of zinc in chemical combination, which does not injure the strength of the fibre, but enables it to resist mildew: Alumina is another metallic oxide, for which ligneous fibre, in its various states and forms, possesses a peculiarly energetic attraction, the important bearings of which upon the arts of color-making, calico-printing, and dyeing, will be afterwards evident. (See also p. 1108.)

When large and especially dense pieces of timber are to be thus impregnated, there is often considerable difficulty in sufficiently permeating them with the metallic solution; for even after long steeping in it, they only become superficially imbued; and although this is in many cases an adequate protection, it is obvious that the greater the depth to which the preservative liquor penetrates, the greater will be the durability conferred. In some cases this penetration has been effectually promoted by placing the wood and preservative liquor in a vessel admitting of being exhausted, so that during the exhaustion, the interstitial air retained in the pores of the wood makes its escape, and is replaced by the metallic solution, on restoring the external pressure.

Another method of effecting a more entire penetration, consists in rendering the natural functions of the tree available for the purpose: the force with which the sap rises from the roots to the leaves is well known, and accordingly, if a tree in full leaf and vigor be cut through just above the root, and the cut surface of the trunk immediately immersed in the metallic solution, this will be carried upwards by the circulating powers of the vegetable and so be transmitted even to the smaller branches and leaves. Even a hole bored into the body of the tree, or a section into it by a saw,



may be resorted to as means of presenting an absorptive surface to which the protective liquor may be applied. It has also been proposed to apply this system to coloring and perfuming woods, by causing them to absorb colored liquors, or metallic solutions, which by reacting upon each other would cause the deposition of colored precipitates; Prussian blue, chromate of lead, tannate of iron, ferrocyanide of copper, and other similar metallic colors have thus been formed in the ligneous texture, and it has been similarly pervaded by certain essential oils. (BOUCHERIE, *Ann. Ch. et Ph.*, LXXIV. 113.) Tannin, empyreumatic oils, kreasote, resinous solutions, and several other materials, have also been employed as means of preserving wood, and of changing and indurating its texture. Those siliceous solutions known under the name of water-glass, and solutions of certain phosphates, have also been thus employed, with the twofold object of preservation from decay and protection from fire (p. 1129).

PRODUCTS OF THE DECAY, EREMACAUSIS, or MOULDERING OF WOODY FIBRE. Wood is subject to several kinds of decay, some of which seem at first sight to relate merely to texture, whilst in others the changes are evidently of a more intricate nature, and terminate in the production of a brown or black pulverulent matter. When wood is preserved in a dry place and atmosphere, or when it is entirely submerged in deep water, it is very little prone to change. In mummy cases, in some ancient buildings, in the piles of bridges, and in certain instances of submerged forests, it has remained almost unchanged in composition and properties for many centuries; but under the influence of the joint action of air and moisture, it undergoes a series of successive changes, affecting both form and composition. Under these circumstances it becomes friable, often of a pale or deep brown color, and, if moist, it converts the oxygen of the air about it, into carbonic acid. The rapidity of these changes, and their concomitant results, depend much upon the nature of the wood in question; that is, upon the quality and quantity of the foreign matters which may have been associated with it, some of which may tend to promote, others to retard the change; certain azotised matters, and perhaps some forms of tannin, are among the former, whilst resins and some of their associates may be among the latter. Beech, chesnut, and oak, as often seen in old forests or parks, or in the timbers of buildings, furnish good specimens of this species of decay; they are of various shades of grey, or brown, and sometimes nearly black, and the resulting product appears to differ in composition with the circumstances under which it has been produced. The decayed wood of oak has been examined by Will and Meyer, with the following results:

|              | Dark brown from the interior<br>of a hollow oak. | Pale brown<br>from another oak. |
|--------------|--|---------------------------------|
| Carbon ..... | 56·212   | 53·36                           |
| Water .....  | 43·789   | 46·44                           |

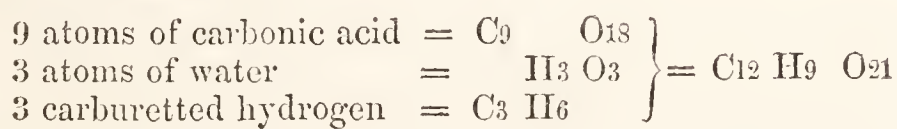
Liebig observes, in reference to these analyses, that if we compare them with recent oak wood, they will stand as follows:

|                                     |             |
|-------------------------------------|-------------|
| A. Recent wood of a sound oak ..... | C36 H22 O22 |
| B. Dark brown decayed.....          | C35 H20 O20 |
| C. Pale brown decayed .....         | C34 H18 O18 |

and from these comparisons, he concludes that it is the hydrogen which is oxidized by the oxygen of the air, and that the evolved carbonic acid is formed at the expense of the elements of the wood; for, as he justly observes, the longer the decay has operated, the greater is the relative proportion of carbon in the residue; and it is seen in the preceding cases, that for every *two* equivalents of hydrogen oxidized by the air, *one* equivalent only of carbon is separated in the form of carbonic acid: so that  $C_{36} H_{22} O_{22}$  becomes  $C_{35} H_{20} O_{20}$ , and not  $C_{35} H_{22} O_{22}$ , as would have been the case had the atmospheric oxygen combined directly with the carbon instead of with the hydrogen of the wood. Supposing this kind of decay to continue till the whole of the hydrogen had been removed, the final solid residue would be carbon only; and this seems to have been the case in the formation of certain kinds of coal, which, like *anthracite*, are little else than pure carbon. In some instances too, the decay of lignine under the joint action of air and water, leads to a similar result; for the black mud of shallow ponds surrounded by trees, and in which a large accumulation of dead leaves and wood has been allowed to rot and decompose, is found to contain a considerable proportion of charcoal. If from the formula of wood,  $C_{36} H_{22} O_{22}$ , we subtract the 22 atoms of oxygen and 11 atoms of the carbon, (forming 11 atoms of carbonic acid,) together with the 22 atoms of hydrogen which are supposed to be oxidized by the atmosphere and separated in the form of water, 25 atoms of carbon will be the final product of the decay. "In other words," says Liebig, "100 parts of oak, which contain 52.5 of carbon, will leave 37 parts of carbon as a residue, which must remain unchanged, inasmuch as carbon does not combine with oxygen at common temperatures. But generally speaking, this final result is not arrived at, for the affinity of carbon for hydrogen seems to increase in proportion as the quantity of the latter diminishes, so that all the common varieties of coal retain hydrogen and oxygen." Wood coal or brown coal, according to an analysis cited by Liebig, may be represented by  $C_{33} H_{21} O_{16}$ ; that is, as containing more carbon and hydrogen, and less oxygen, than wood; for if wood were to lose three atoms of carbonic acid and one atom of hydrogen, brown-coal, composed as above, would be the result: wood =  $C_{36} H_{22} O_{22} - 3CO_2, H = C_{33} H_{21} O_{16}$ . Splint coal and cannel coal, according to the analyses of Richardson and Regnault, are  $C_{24} H_{13} O$ , and may be derived from wood by the abstraction of carbonic acid and hydrogen; thus

Wood is ..... =  $C_{36} H_{22} O_{22}$

And if from this we deduct



The remainder is *coal*, composed of



"The separation of carbonic acid," says Liebig, "seems still to go on even in the deepest beds of brown coal, and is the source of the acidulous springs found near such beds, and also of the choak-damp of the mines of wood coal; whereas in other cases carburetted hydrogen or fire-damp is found predominant, especially in the mines of common caking coal,



which is  $C_{20}H_9O$ , or cannel coal *minus* olefiant gas; and what is termed the *fire-damp* of coal mines, always contains, according to Bischoff, olefiant gas, as well as light carburetted hydrogen and carbonic acid." (TURNER'S *Chemistry*, edited by Liebig and Gregory, p. 1175; and LIEBIG'S *Organic Chemistry in its applications to Agriculture and Physiology*, 1840, p. 324.)

HUMINE. GEINE. ULMINE. HUMIC ACID. ULMIC ACID. These terms have been applied to the peculiar brown matter which may be extracted from bog-earth, peat, and turf, and which is found as a more or less abundant ingredient in soils, where it is derived from the slow decay of plants: it is also contained in the brown decayed woods above adverted to; and there is a brown exudation found upon the barks of trees, and especially of the *elm*, and hence called *ulmine*, which contains a similar matter combined with potassa. Lastly, the action of heat, acids, alkalis, and some other chemical agents, upon a variety of organic substances, is attended by the formation of a similar product. As it combines with bases, Boullay terms it *ulmic acid*; and according to him, the brown matter occasionally produced by the decomposition of hydrocyanic acid (p. 513), contains it united with nitrogen; this he calls *azulmic acid*. (*Ann. Ch. et Ph.*, xliii. 273.) He represents ulmine, or ulmic acid, as a compound of 56·7 *per cent.* of carbon, and 43·3 *per cent.* of hydrogen and oxygen in the proportions to form water: he considers it as a most important ingredient in the soil as relates to its nutritive powers, for in its moist state it produces carbonic acid, and it seems to have a peculiar tendency to condense or absorb ammonia. Malaguti has already been quoted (p. 1186), as having obtained a peculiar black crystalline substance by the long-continued action of very dilute nitric acid upon sugar at a boiling heat; this has been regarded as *crystallized ulmic acid*.

*Ulmine*, or *ulmic acid*, may be obtained by digesting the brown exudation of the elm in boiling water, and precipitation by an acid. Rotten leaves, bog-earth, wood-soot, peat, or turf, may be digested in a weak solution of caustic or carbonated potassa, by which a brown liquid is obtained (*ulmate of potassa*), from which acids also throw down ulmine. Braconnot procures it (*Ann. Ch. et Ph.*, xii. 192) by heating equal weights of caustic potassa and sawdust, or shavings of wood, with a little water, in a silver crucible, continually stirring the mixture: when it suddenly boils up, it is removed from the fire, and stirred till cold, so as to expose it as much as possible to the air, for the formation of ulmic acid in this case depends upon the absorption of oxygen. When cold, the product is dissolved in water, filtered, and decomposed by dilute sulphuric acid; the precipitated ulmic acid is then washed and dried. According to Peligot, the intervention of air in this operation is unnecessary, and if potassa and humid lignine, along with a little mercury to equalize the temperature, be heated up to the boiling-point of mercury, aqueous vapor, and then hydrogen, is disengaged, and ulmic acid formed. But the characters of the ulmic acid vary with the temperature, and it is far from being the only product of the reaction, for pyroligneous spirit, oily products, and formiate, oxalate, and carbonate of potassa are at the same time formed.

According to the analyses of Mulder, all the ordinary forms of humine or ulmine contain ammonia, and therefore yield nitrogen as an ultimate element. The varieties of *humine* have consequently been represented as *salts of ammonia*, and a variety of formulæ have been imagined as the representatives of these supposed compounds; but they are at such variance with each other, and so manifestly hypothetical, as to deserve no confidence. Mulder's formulæ for two of these combinations of humic acid and ammonia, namely, from turf and from mould, are as follow:

|                  |                               |
|------------------|-------------------------------|
| From turf .....  | $C_{40} H_{12} O_{12} + NH_3$ |
| From mould ..... | $C_{40} H_{12} O_{14} + NH_3$ |

The precipitates produced by acids in alkaline solutions of the varieties of humine, differ in appearance and properties with the source whence they are derived: the substance which is thrown down is generally in the form of a brown flocculent matter, which when dried becomes brittle and resin-like. It is nearly tasteless, almost insoluble in water, but communicates a light-brown tinge to it: sulphuric acid dissolves it, but lets it fall on dilution, and the precipitate then retains a little of the acid: it combines and forms soluble compounds with the alkalis: with the alkaline earths, and many of the other oxides, it produces combinations which are insoluble or difficultly soluble in water; but the characters of these compounds, as given by different authorities, are much at variance. Some of the metallic salts precipitate it so completely as to leave the supernatant liquid colorless; and certain of its compounds form useful pigments (*umbers* are of this description?) and may be employed in dyeing and calico-printing.

There can be no doubt of the importance of humine as an ingredient of soils, contributing to their fertility; but not, as formerly supposed, by being absorbed, and acting directly as nutriment to the growing vegetable, but as slowly evolving carbonic acid, and attracting or fixing ammonia, and thus, indirectly furnishing carbon, hydrogen, oxygen, and nitrogen, in those forms in which they are taken up by the roots and leaves of the growing plant.

CRENIC ACID. Under this term (from *κρηνη*, a fountain), Berzelius has described a species of extractive matter which he found in the water of Porla well, near Orebro, in Sweden. This water has a yellow color, and deposits an ochraceous sediment, which is a *crenate of peroxide of iron*. To another form of extractive matter found in the same water, he has given the name of *apocrenic acid*. (*Poggend.* xxix. THOMSON. *Chem. of Organ. Bodies*, 147.) An analogous substance has been described by Haenle, under the name of *Puteanic acid*. (*Journ. de Pharm.*, xxi. 310.)

EXTRACTIVE MATTER. Under the term *brown extractive matter*, or *extract*, the pharmaceutical chemists originally included all substances capable of being extracted from vegetable products by decoction in water, and afterwards obtained in a solid form by evaporation. Such extracts might of course contain many of the substances described in the foregoing sections, and others afterwards to be mentioned; their properties were therefore extremely various and indefinite. They afterwards endeavoured to distinguish the varieties by the terms *bitter*, *sweet*, *mucilaginous*, *astringent*.



*gent, narcotic, coloring, and resinous extracts, &c.*; but in general, any brown residue obtained by boiling down the decoctions, or infusions, or even the expressed juices of vegetables, was distinguished by the generic term *extract*. Boerhaave first pointed out the existence of a peculiar substance in these extracts, soluble both in alcohol and in water, which he called *Materia hermaphrodita*; Scheele called it *Materia saponacea*; and Vauquelin afterwards gave the name *extractive matter* to what he regarded as a peculiar vegetable principle, soluble in water and in alcohol, insoluble in ether, and becoming insoluble in water by long-continued boiling, and by exposure to light and air.

It seems probable that the *brown extractive*, obtained by the above processes, is not pre-existent in the vegetables whence it is obtained, but partly at least a *product* of the action of heat, water, air, and other agents, upon some of their other proximate principles. The different *coloring-matters* of plants have also been termed *colored extractive*, but these we shall consider separately. It will also be found in regard to many of the pharmaceutical extracts, that their activity resides in some peculiar and distinct proximate principle, mixed with other unimportant and inactive substances. Such principles will afterwards be separately considered\*.

**PIT COAL.** Although no mention is made of the presence of *nitrogen* in the analyses of coal already quoted, it is a curious fact that that element is always found as a constituent of the common varieties of pit coal; its relative proportion to the other elements is subject to much variation, but, as the production of humine is in many instances connected with the formation of coal, and as such humine is almost always associated with ammonia, it may perhaps be derived from that source. The origin of this ammonia has been by some exclusively referred to the decomposition of the azotized principles existing in the vegetables, to the *eremacausis* of which, the production of the humine has been ascribed; but independent of this, it has already been remarked, that humine, and some analogous substances, are gifted with a peculiar absorptive power in regard to ammonia, by which they are enabled to receive and retain it.

There are three chemical varieties of pit coal. 1. The first or *brown coal*, retains some remains of the vegetables from which it has originated. When heated, it exhales a bituminous odor, and burns with a clear flame. It is generally of a tough consistence, and yields, according to Hatchett, a portion of unaltered vegetable extract and resin. 2. The second variety, or *black coal*, is the ordinary fuel of this country. It exhibits few or no traces of vegetable origin, and consists principally of bitumen and charcoal,

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\* In preparing *extracts* for pharmaceutical use, the greatest care must be taken to avoid injuring them by heat, and they should accordingly be evaporated in a water-bath, or by steam not exceeding 212°. It is easy to evaporate at lower temperatures, as in vacuo, or even over sulphuric acid, and many of the extracts used in medicine may be so obtained, of much

greater activity than when prepared in the usual way: but for medical use this is perhaps not desirable; *uniformity* is the great object, and whether half a grain or two grains of the more powerful extracts is a dose, is of less importance than the certainty that they are, as far as possible, of a given power.

in variable proportions. When exposed to heat it swells, softens, and burns with a bright flame, leaving a small quantity of ashes. Many varieties, however, abound in earthy matter, and these produce copious cinders, and burn with a less intense heat. The products of the destructive distillation of this kind of coal have been already described. (p. 493.) The residue is a hard, sonorous charcoal, termed *coke*, (p. 449,) and containing the earthy ingredients of the coal. 3. The third variety, *anthracite*, or *glance coal*, consists almost entirely of carbon and earthy matter. It burns without flame, and, when distilled, yields scarcely any gaseous products. Two specimens of anthracite, analysed by Vanuxen, (*Silliman's Journ.*, x. 102,) afforded 90 *per cent.* of charcoal, from 3 to 5 of earthy matter, and 4 to 6 *per cent.* of water. All the varieties of common coal, as has already been stated, afford ammonia when subjected to destructive distillation, and in consequence of the enormous quantities of pit coal distilled for the production of illuminating gas, a large part of the commercial demand for ammoniacal salts is now supplied from that source.

Dr. Thomson arranges the different kinds of British coal under the following divisions. (*Ann. of Phil.*, xiv. 81.) 1. *Caking coal*; 2. *Splintery coal*; 3. *Cherry coal*, which is less hard and more slaty in fracture; 4. *Cannel coal*, such as that from Wigan in Lancashire. These varieties he states to be composed as follows:—

|                | Caking coal. |      | Splint coal. |      | Cherry coal. |      | Cannel coal. |  |
|----------------|--------------|------|--------------|------|--------------|------|--------------|--|
| Carbon .....   | 75·28        | .... | 75·80        | .... | 74·45        | .... | 64·72        |  |
| Hydrogen ..... | 4·18         | .... | 6·25         | .... | 12·40        | .... | 21·56        |  |
| Nitrogen ..... | 15·96        | .... | 6·25         | .... | 10·22        | .... | 13·72        |  |
| Oxygen .....   | 4·58         | .... | 12·50        | .... | 2·93         | .... | 0·00         |  |
|                | <hr/>        |      | <hr/>        |      | <hr/>        |      | <hr/>        |  |
|                | 100·00       |      | 100·00       |      | 100·00       |      | 100·00       |  |

The proportion of nitrogen here given appears enormous. Regnault, in his laborious researches on the composition of the mineral combustibles, never found more than from 1·5 to 2 *per cent.* (*Ann. Ch. et Ph.*, lxvi. 365.) But the analyses of coal are extremely discordant. Dr. Ure, for instance, (*Phil. Trans.*, 1822, p. 467,) obtained the following results:—

|                | Cannel coal. |      | Splint coal. |  |
|----------------|--------------|------|--------------|--|
| Carbon .....   | 72·22        | .... | 70·90        |  |
| Hydrogen ..... | 3·93         | .... | 4·30         |  |
| Nitrogen ..... | 2·80         | .... | 0·00         |  |
| Oxygen .....   | 21·05        | .... | 24·80        |  |
|                | <hr/>        |      | <hr/>        |  |
|                | 100·00       |      | 100·00       |  |

Dr. Henry regards Dr. Ure's results, as far as concerns the oxygen, to be the most correct, but he always obtained *ammonia* from both the above varieties of coal, and therefore infers the existence of nitrogen, though not to the extent given by Dr. Thomson. The following are Dr. Thomson's results, as to the volatile products, coke, and ash, in

|                                 |     | Volatile products. |     | Weights of coke. |     | Incombustible ash. |
|---------------------------------|-----|--------------------|-----|------------------|-----|--------------------|
| 1000 parts of caking coal ..... | 226 | ....               | 774 | ....             | 15  |                    |
| „ splint coal .....             | 352 | ....               | 647 | ....             | 95  |                    |
| „ cherry coal .....             | 477 | ....               | 522 | ....             | 100 |                    |
| „ cannel coal .....             | 600 | ....               | 400 | ....             | 110 |                    |



The *ashes* of coal and coke are composed as follows:—(FOWNES, *Journ. Agric. Soc.*, iv. 541.)

|   | Staffordshire<br>coal. |      | Newcastle<br>coal. |      | Staffordshire<br>coke. |
|---|------------------------|------|--------------------|------|------------------------|
| Sandy matter and unburned charcoal ....                                 | 64·0                   | .... | 87·6               | .... | 76·8                   |
| Oxides of iron and manganese; alumina<br>and some phosphoric acid.....} | 9·8                    | .... | 3·6                | .... | 7·0                    |
| Carbonate of lime .....   | 12·8                   | .... | 1·0                | .... | 4·6                    |
| Sulphate of lime .....  | 2·44                   | .... | 0·54               | .... | 3·8                    |
| Alkaline sulphate with trace of chloride<br>and sulphuret .....         | 0·4                    | .... | 1·26               | .... | 0·8                    |
| Water, trace of magnesia, and loss .....                                | 10·65                  | .... | 6·00               | .... | 7·0                    |
|   | <hr/> 100·00           |      | <hr/> 100·0        |      | <hr/> 100·0            |

The following comparative table of the composition of *turf*, *lignite*, and different kinds of coal, has been drawn up by Kane (*Elem. of Chem.*), from the results of the analyses of Richardson and Regnault.

| Kind of fuel.    | Carbon. |      | Hydrogen. |      | Oxygen<br>and nitrogen. |      | Ashes. |      | Economic value<br>of 100 parts. |
|------------------|---------|------|-----------|------|-------------------------|------|--------|------|---------------------------------|
| Turf .....       | 58·09   | .... | 5·93      | .... | 31·37                   | .... | 4·61   | .... | 171                             |
| Lignite.....     | 71·71   | .... | 4·85      | .... | 21·67                   | .... | 1·77   | .... | 208                             |
| Splint coal .... | 82·92   | .... | 6·49      | .... | 10·86                   | .... | 0·13   | .... | 262                             |
| Cannel coal .... | 83·75   | .... | 5·66      | .... | 8·04                    | .... | 2·55   | .... | 260                             |
| Cherry coal .... | 84·84   | .... | 5·05      | .... | 8·43                    | .... | 1·68   | .... | 258                             |
| Caking coal .... | 87·95   | .... | 5·24      | .... | 5·41                    | .... | 1·40   | .... | 271                             |
| Anthracite ....  | 91·98   | .... | 3·92      | .... | 3·16                    | .... | 0·94   | .... | 273                             |

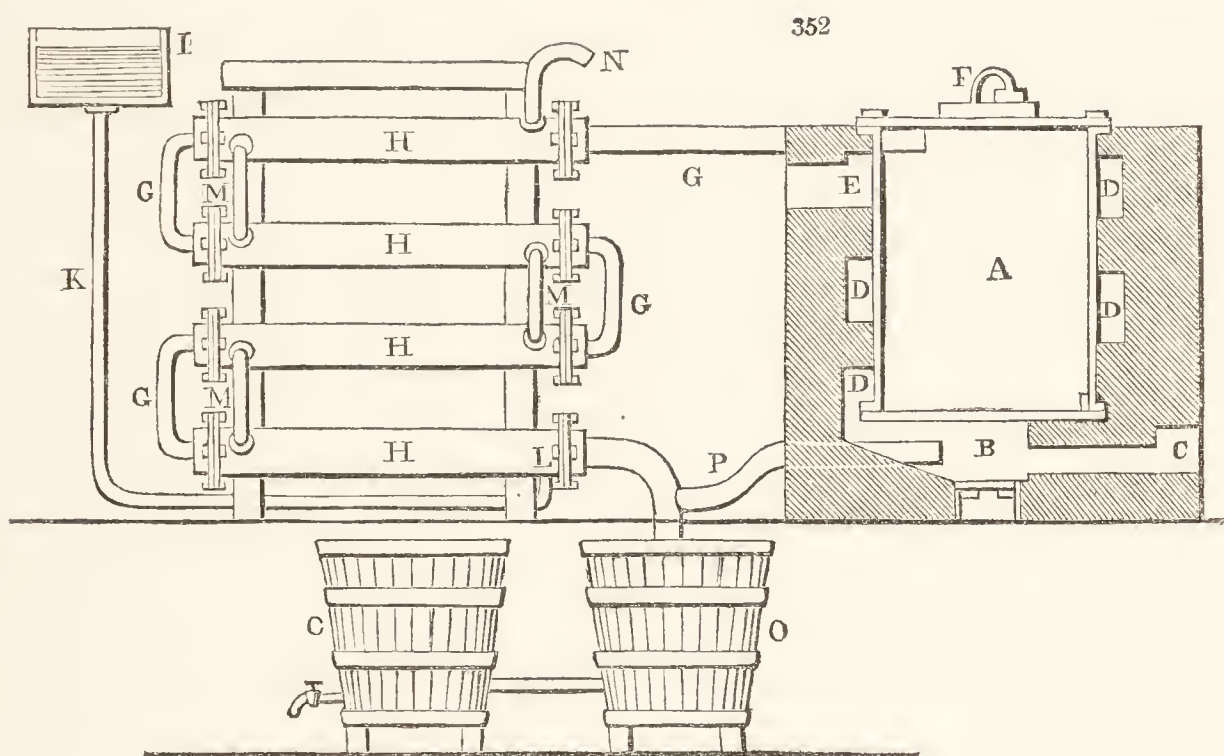
The above results would have been much more valuable, had the *nitrogen* been separately estimated; and again, in almost all these analyses of coal, *sulphur* is generally omitted; it is, however, so uniformly present as to deserve enumeration amongst the ultimate elements of pit coal, though the state, or combination in which it exists, is often not evident, for it is found in coal in which no traces of *pyrites* are visible.

PRODUCTS OF THE DESTRUCTIVE DISTILLATION OF WOOD. These products are, under all circumstances, extremely complicated and multifarious, and they vary considerably with the nature of the wood, and the temperature, and other circumstances under which the distillation is effected. Some kinds of wood abound in resin, and in such cases the results of its distillation are largely blended with the peculiar products arising out of the decomposition of that substance, some of which have already been noticed (p. 494), and others will be afterwards adverted to. Other woods are comparatively abundant in azotised principles, and in such cases ammonia is, to a greater or less extent, combined with their pyrogenic products. The products of the distillation of the white woods, such as are free from resin, and those commonly used as sources of charcoal, have been most accurately examined, and we shall select these as probably furnishing the nearest approach to the results which would be obtained by operating upon pure woody fibre.

When these woods are placed in retorts gradually heated up to bright redness, the products which pass over are partly gaseous, and partly condensable vapors; and charcoal, with small quantities of other fixed substances, constitute the residue. The gases are such as have already been noticed, namely, certain varieties of carburetted hydrogen, together with carbonic acid and oxide; and the vapors condense partly into liquid and partly solid products. The liquids are partly soluble, and partly inso-

luble in water, the former being chiefly pyroxylic spirit, acetic acid, and substances allied to them, which will be noticed afterwards; and the latter constituting tar and certain oily substances. These latter, and their accompanying solid products, we may now proceed to examine.

The apparatus used for the wholesale distillation of wood, varies according to the nature of the products which are principally required: the following form of furnace, retort, and condenser, will give some notion of the process as it is most usually conducted, where the object is to obtain pyrolignous acid and spirit, or to procure the varieties of charcoal (p. 444,) which are preferred by the manufacturers of gunpowder (p. 578,) and which are exclusively derived from white woods. (KANE, *Elem. Chem.*, 1088; URE, *Dict. of Arts, &c.*, Art. *Pyrolignous Acid*.)



A is a cast-iron cylinder built into a furnace, of which B is the fire-place, C the fire door, D the flue, which winding spirally round the cylinder so as to heat it as uniformly as possible, terminates in the chimney at E. The wood, cut into proper billets, is introduced by an opening in the top plate at F, which admits of being securely closed. The gaseous and other volatile products pass off through the tube G, which is bent zigzag, and surrounded, by larger tubes, H, which convey a current of cold water, supplied from a reservoir at I, and which, flowing down the tube K, enters the system of condensers at L, and passing from one water-tight jacket to another by the cross pipes M, escapes ultimately nearly at a boiling heat at N. The liquids which are thus condensed consist of tar, and water holding pyroxylic spirit, acetic acid, and other matters in solution, and these are collected in the tubs O, whilst the gases which are generated pass through the tube P into the ash pit, where they are burned, and serve to economise fuel.

**TAR.** Two kinds of tar occur in commerce, namely, *Coal Tar*, the principal components of which have already been noticed, in the section on *Carbon*, (p. 502,) and *Wood Tar*, of which there are two varieties, one known as *Stockholm Tar*, obtained from the waste of fir timber; and the other, as the tar of the wood-vinegar and gunpowder works. Wood tar is



brown or black, acid, of a thick consistency, and a strong and peculiar odor varying with its source. When distilled it yields a variety of products, and leaves a dark-brown or black residue called *pitch*. It has been frequently the subject of experiment, but has lately acquired peculiar interest from the researches of Reichenbach, who has obtained from it several definite compounds, of which the most remarkable are the following:—

1. PARAFFINE. When beech tar is distilled, three liquids pass into the recipient: 1. a light oil; 2. an aqueous acid; 3. a heavy oil. The *heavy oil* is subjected to several redistillations, and then sulphuric acid is gradually added to it, till the mixture becomes a black and thin liquid; and if it does not spontaneously rise in temperature to  $212^{\circ}$ , it is to be heated up to that point: the mixture is then kept for twelve hours, or more, at a temperature of about  $122^{\circ}$ , when a colorless oil will be found floating upon its surface, which is to be carefully poured off, and, on cooling, the *paraffine* concretes upon its surface: it is to be removed, washed, and pressed in folds of bibulous paper, and finally purified by solution in hot anhydrous alcohol, from which it separates, on cooling, in a solid form; it is somewhat flexible, and not greasy; crystalline, tasteless, colorless, and odorless: at  $112^{\circ}$  it fuses into a transparent oily liquid, and at a higher temperature boils and distils without change: its vapor burns with a white sootless flame. Its specific gravity is 0.870. Its name is derived from its inertness as a chemical agent, or its want of affinity (*parum affinis*). (*Schweigger's Journ.*, Lix. 436: Lxi. 273. Lxii. 129.) It resists the action of acids, alkalis, chlorine, and potassium, and cannot be united by fusion with camphor, naphthaline, benzoin, or pitch; but it unites with stearine, cetine, bees'-wax, and colophony, and readily dissolves in oil of turpentine and in naphtha. 100 parts of ether dissolve 140 of paraffine at the temperature of  $75^{\circ}$ ; at a lower temperature the solution concretes into a white crystalline mass. It separates from its hot alcoholic solution in crystalline laminae, when not too concentrated. According to J. Gay Lussac (*Ann. Ch. et Ph.*, L. 78), it is a binary compound of carbon and hydrogen, and its elements are in the same ratio as those of olefant gas, &c., but as the density of its vapor has not been determined, its atomic constitution, and its equivalent, remain unascertained. Paraffine appears to exist in the fossil wax of Moldavia (MAGNUS, *Ann. Ch. et Ph.*, LV. 217), and in the product of the distillation of bituminous schist. (LAURENT, *Ibid.*, LIV. 392.) It exists in large quantity in Rangoon petroleum, and is formed during the distillation of wax.

EUPION. This liquid was also discovered by Reichenbach. (*Poggend.*, xxiv. 173. *Ann. Ch. et Ph.*, L. 69.) It is associated in common tar with paraffine; but it is most abundant in *animal tar*, especially that obtained from horn or bones. This tar is distilled, so as to yield about three-eighths: this last product is mixed with an eighth of sulphuric acid, and the lighter yellow liquid which then separates is poured off, mixed with its weight of sulphuric acid, and distilled: a colorless liquid passes over, which is to be mixed with a solution of potassa; after some time it separates upon the surface of the mixture, when it is to be poured off, mixed with a fourth its weight of sulphuric acid, and again distilled, washed with hot solution of potassa, decanted off as before, and

slowly distilled with water till three-fourths have passed over: this ultimate product is placed in vacuo for 24 hours, then heated to its boiling-point with a few grains of potassium, and when it no longer is at all acted on by that metal, it is allowed to cool and poured from the deposits: it is then *eupion*. If it contain paraffine, the two may be separated by distillation with water, and the first portions which pass over are then entirely free from it.

Eupion may also be obtained by the distillation of rape-seed oil in an iron retort: the first and last portions are rejected: the middle portion has the sp. gr. 0·86, which by redistillation may be lowered to 0·74, and if it be then mixed with oil of vitriol and redistilled, and the product washed with solution of potassa, and carefully rectified off chloride of calcium, its specific gravity is reduced to about 0·70, and is said by Reichenbach to be pure eupion. (*Journ. für prak. Chem.* I. 377.)

Eupion is tasteless, colorless, inodorous, very limpid, specific gravity 0·65; it remains liquid at  $-4^{\circ}$ , and boils at about  $340^{\circ}$ , distilling over without change. It is a non-conductor of electricity. Its vapor burns with a pure white flame. It is insoluble in water. 100 parts of alcohol at  $66^{\circ}$ , dissolve 33 parts, but at a lower temperature the greater part of the eupion separates. Acetic ether dissolves about a third of eupion; sulphuret of carbon, oil of turpentine, naphtha, and almond and olive oil readily mix with it; it dissolves chlorine and bromine, and again evolves them when heated: with iodine it forms a blue solution: aided by heat it dissolves phosphorus, sulphur, and selenium, but deposits the greater portion on cooling. It dissolves naphthaline, camphor, stearine, cetine, cholesterine, and paraffine, at common temperatures, and more abundantly when heated. Caoutchouc swells in it, and dissolves when heated, but the solution remains glutinous when spread upon a surface, except it be dried by heat. The acids and alkalis are without action on eupion, and it is not altered by exposure to air. It has not been satisfactorily analyzed; at least the results obtained by Laurent and by Hesse, are somewhat at variance. (*Ann. Ch. et Ph.*, Lxiv. 326. *Ann. der Pharm.*, xxiii. 247.) It most probably is a hydrocarbon  $= \text{CH}$ . Its name is derived from *ευ*, *well*, and *πιων*, *greasy*, for it has the greasiness of a fixed oil.

KREASOTE, or CREASOTE, (from *κρεας*, *flesh*, and *σωζω*, *I save*.) This interesting product was discovered also by Reichenbach. (*Ann. Ch. et Ph.*, Liii. 325.) It is obtained from *wood tar*, which is subjected to distillation till the residue has the consistency of pitch; but the process should not be urged too far. *Oil*, and acid water pass over; the former is separated, and distilled in a glass retort (not to dryness), when two products are again obtained, of which the acid water is rejected as before, and the oil preserved. In these distillations, the oil which first passes over is lighter than that which succeeds, its density augmenting with the heat: the lighter oil contains but little kreasote, and consists chiefly of eupion and lighter products: the *heavy* portion is pale-yellow, but becomes brown by exposure to air; it has a disagreeable odor, and tastes caustic, sour, sweet, and bitter. To this heavy oil, carbonate of potassa is added as long as it effervesces; it is then poured off from the produced acetate of potassa and redistilled (not to dryness:) the lighter part is again rejected, and the heavy oil is now dissolved in a solution of caustic



potassa of the specific gravity 1.12: heat is evolved, and an insoluble compound of eupion, and other oils, floats upon the surface and is removed. The alkaline solution is then gradually heated in an open capsule to its boiling-point; it rapidly absorbs oxygen, and becomes brown; it is suffered to cool in the air, and then dilute sulphuric acid is added, which causes the oil to separate. This oil is now mixed with water and a little caustic potassa, in a retort, and the mixture subjected to rapid ebullition; but in consequence of the feeble tension of kreasote vapor at  $212^{\circ}$ , it passes slowly over; at length a period arrives when, although much oil remains in the retort, but little passes over, notwithstanding the heat is raised: it is then time to stop the process; the residue contains *picamar*, sulphate and acetate of potassa, and a brown substance.

The oil in the receiver is now separated from the water, and again dissolved in solution of potassa: a portion of light insoluble oil separates as before, which being removed, the mixture is again heated in an open vessel, and as it slowly cools it again becomes brown, but less so than formerly; sulphuric acid is then added in slight excess, and the evolved oil is washed, as long as it is acid, with cold water. The distillation of this oil with water is again repeated, but, instead of adding potassa, a little phosphoric acid is employed to abstract a portion of ammonia which the oil still retains. The distilled oil is now, for the third time, dissolved in the caustic potassa, and if the precautions above described have been attended to, they combine without the separation of any oily matter, and the mixture, exposed to air, only acquires a slight red tinge. When the kreasote is now ultimately separated from its combination with the potassa, it is sufficiently pure for medical use: to obtain it absolutely pure, it must be distilled with water, and this hydrated product again rectified: water first goes over, and afterwards, at a high temperature ( $203^{\circ}$  Cent.), the kreasote: to deprive it absolutely of water, its vapor must be passed over chloride of calcium.

I have taken the above details from Dumas: the process, though not difficult, is, as he observes, very troublesome, but methods of improving and facilitating it will doubtless be discovered. It has been, to a certain extent, simplified by Hubschmann. (*Ann. Ch. et Ph.*, lvii. 105.)

Kreasote, when pure, is a colorless transparent liquid, of great refractive and dispersive power; it has a penetrating and strong odor resembling that of smoked meat, and a burning caustic taste: its specific gravity is 1.037 according to Reichenbach; (1.060 CHRISTISON) at  $65^{\circ}$ ; it boils at  $397^{\circ}$  ( $203^{\circ}$  Cent.), and retains its fluidity at  $-17^{\circ}$ . It is a non-conductor of electricity, and it burns with a very sooty flame. When mixed with water, two solutions result; the one consisting of 1.25 kreasote + 100 water; the other, of 100 kreasote + 10 water. The aqueous solution is neither acid nor alkaline.

Pure kreasote dissolves oxide of copper, forming a brown solution: when boiled with peroxide of mercury, metallic mercury separates, and the kreasote is converted into a resin: it gives a blue tint to very dilute solutions of the persalts of iron. It produces effervescence and red fumes with nitric acid. It absorbs chlorine, and is gradually changed by it into a resin. It is colored by bromine, iodine, sulphur, and phosphorus. With potassium it evolves gas, and potassa is formed, which combines with the kreasote. It is thickened and blackened by concen-



trated sulphuric acid. Acetic acid is its most perfect solvent. It forms two compounds with potassa; the one anhydrous, liquid, and of an oily consistence; the other hydrated, and crystallizable in nacreous plates. All the acids decompose these compounds, and separate unaltered kreasote. With soda it produces similar combinations. It also combines with ammonia, lime, and baryta. It dissolves many salts. Alcohol, ether, sulphuret of carbon, eupion, naphtha, and acetic ether, dissolve it in all proportions. It does not combine with pure paraffine. It dissolves the resins, camphor, essential oils, and almost all coloring matters, including those of cochineal, saunders-wood, dragons'-blood, madder, saffron, and, with the aid of heat, indigo. Its action upon caoutchouc, unlike that of eupion, is very feeble.

Kreasote immediately coagulates egg-albumine, although much diluted; it also coagulates serum. Meat and fish are preserved after having been brushed over with kreasote and dried in the sun; and it appears to be the principle to which the antiseptic powers of wood-smoke, and pyroligneous acid are due. A patent has been taken by Mr. Fitch for the impregnation of salt with the more volatile products of wood-tar: the salt thus prepared is doubly preservative, so that meat to which it is applied is at once smoked and salted. Tongues and hams may be effectually cured by immersing them for twenty-four hours in a mixture of 1 part of pure kreasote and 100 of water or brine; and when thus prepared they have the delicate smoked flavor observed in rein-deer tongues as usually cured by smoking. (GREGORY.) The action of kreasote upon the animal system is energetic; it is painful upon the tongue and destroys the epidermis; it kills fishes and insects: it also destroys vegetation. It is medicinally employed in toothach, cancer, ulcers, and cutaneous diseases, externally; and to check hæmorrhage; and internally as a stimulant and for the prevention of nausea and vomiting. Three or four drops, added to a pint of ink, effectually prevent its mouldiness. According to Ettling, (*Ann. Ch. et Ph.*, liii. 333,) it consists of 77.42 carbon, 8.12 hydrogen, 14.46 oxygen; but, as it probably retains a variable portion of water, its atomic constitution cannot be accurately inferred. Deville gives the formula  $C_{28}H_{16}O_2 = 2$  volumes of kreasote vapor. (*Ann. Ch. et Ph.*, October, 1844.) Dr. Gregory observes that there is a great resemblance between kreasote and carbolic acid (p. 502), and is inclined to consider kreasote as a somewhat impure carbolic acid. "The taste, smell, density, (according to some) boiling-point, solubility in water, poisonous and antiseptic action of these two bodies are the same. Both combine with alkalis forming crystallizable compounds; and what is more important, their composition in 100 parts is almost identical. The chief differences seem to be that carbolic acid may be obtained in crystals, which, however, on contact with the air, instantly liquify and retain the liquid form, without any appreciable change of composition, apparently from the effect of a trace of moisture. Also the salts of carbolic acid with bases are more easily formed and more permanent than those of kreasote. A splinter or shaving of fir wood, dipped into carbolic acid, and then into nitric or hydrochloric acid, becomes first blue and then brown, which does not appear to be the case with kreasote. But Laurent has recently shown that kreasote, when acted on by a mixture of hydrochloric acid and chlorate of potassa, yields abundance of chloranile, a character in which it agrees with carbolic



acid. Both substances also yield nitropicric acid when acted on by nitric acid, although in the case of kreasote this acid is accompanied by others not yet examined. These results I have myself also obtained; and it would appear that if kreasote be not carbolic acid contaminated with some foreign matter, these two bodies are at least closely connected and belong apparently to the same series, which is either that of benzoyle, or that of phenyle. It is not improbable that kreasote may be a definite compound of carbolic acid with some substance of closely allied composition, but of basic properties." (*Outlines*, p. 506.)

PICAMAR. This is the *bitter principle* of tar; whence it derives its name (*Picis amarum*). It is contained in the *heavy oil of wood tar*; that portion, the specific gravity of which exceeds 1.095, is mixed with 8 parts of a solution of potassa, specific gravity 1.15, and left to itself: a layer of impure eupion and paraffine separates upon the surface, after which the liquor clears, and in twenty-four hours deposits brilliant acicular or lamellar crystals; these are dried between folds of blotting paper, and repeatedly dissolved in boiling solution of potassa, till the mother-liquors are colorless, and the crystals buff-colored: they are then decomposed by dilute phosphoric acid, which combines with the potassa, and separates a brownish limpid oil, which, after having been two or three times redistilled with water acidulated by phosphoric acid, is ultimately carefully rectified without addition. The product thus obtained is *picamar*. It is almost colorless and transparent; its consistency is that of oil, and it is greasy. It is insupportably bitter, with an aroma like peppermint; its specific gravity is 1.10 at 65°. It boils at 545°, being less volatile than kreasote. Nitric and hot sulphuric acid decompose it: it dissolves in acetic acid, and is the source of the bitter flavor of crude pyroligneous acid. It is soluble in all proportions in alcohol, and in sulphuric and acetic ether, and in kreasote. It neither dissolves paraffine, asphaltum, nor amber: it takes up caoutchouc when hot, but deposits it again on cooling. It forms crystallizable compounds with potassa, which are almost insoluble in pure alcohol: weak alcohol dissolves the crystals when hot, but deposits them again as it cools. When impure, these crystals gradually become brown or blue. It also combines with ammonia, soda, lime, and baryta, but the bases are not neutralized in any of these compounds. Picamar reduces red oxide of mercury to the metallic state, and minium to the state of protoxide. Its ultimate composition has not been determined.

PITTACAL. When a few drops of baryta-water are added to an alcoholic solution of impure picamar, or even to oil of tar deprived of its acid, the liquor immediately assumes a bright blue tint, which in a few minutes passes into an indigo color. Dumas considers this substance identical with a blue product obtained, in 1827, from coal tar, by MM. Barthe and Laurent. Reichenbach gave it the above name, from *πιττα*, *pitch*, and *καλλος*, *ornament*.

The mode of separating pittacal has not been clearly described: Dumas states, that when precipitated in a flocculent state from its solutions, or obtained by evaporation, it closely resembles indigo, and, like it, acquires a coppery hue when rubbed: it is inodorous, tasteless, and not

volatile: at a high temperature it becomes charred without evolving ammonia. It is decomposed by nitric acid: hydrochloric and dilute sulphuric acid dissolve it; and it is abundantly soluble in acetic acid, forming a red liquid, which, when saturated by an alkali, becomes of a bright blue. Reichenbach represents it as a more delicate test of acids and alkalis than litmus. It is insoluble in alcohol, in ether, and in eupion. With acetate of lead, protochloride of tin, ammonio-sulphate of copper, and acetate of alumina, it yields a fine blue color with a tint of violet: these combinations may probably be useful as dye-stuffs, for they are not affected by air or light. It is said, like indigo, to contain nitrogen, but its ultimate composition has not been accurately determined.

CAPNOMOR, (so termed from *καπνος*, *smoke*, and *μοιρα*, *part*, because it forms part of wood smoke,) is a colorless transparent liquid of a pungent and rather agreeable odor, which occurs with the above products in the heavy oil of tar. (*Journ. de Pharm.*, xxi. 245.) When that oil is digested with solution of potassa, the kreasote, picamar, and pittacal, are taken up, and *capnomor*, with a little eupion, floats upon the surface: this is separated and mixed with sulphuric acid, which dissolves the capnomor and leaves eupion; carbonate of potassa separates the capnomor from its acid combination, and it is purified by distillation. Its specific gravity is 0.977: it boils at 365°, and does not congeal at -6°. It is insoluble in water and the alkalis, but soluble in alcohol, in ether, and in eupion. It dissolves caoutchouc with the same facility as naphtha does. Its composition has not been determined.

CEDRIRET. This compound was also discovered by Reichenbach in oil of tar. The rectified empyreumatic oil obtained by distilling the tar of beech wood was freed from acetic acid by carbonate of potassa, and afterwards digested with a solution of caustic potassa. The alkaline solution thus obtained (freed from all insoluble matters) was saturated with acetic acid, which occasioned the separation of a portion of the dissolved oil, while another portion was retained in solution with the acetate of potassa, from which it was separated by distillation. When about a third part had come over the receiver was changed, and it was tried whether a drop of the oil distilling over produced a red precipitate in a solution of persulphate of iron: as soon as this was the case the product was collected. Its characteristic property is that of being reddened by substances which readily part with oxygen, as also by exposure to air; in the latter case it forms red reticulated crystals (the term *cedriret* applied to them being derived from *cedrium*, an old name for the sour water of tar-burners, and *rete*, a net.) The crystals of cedriret burn with flame, but do not fuse when heated. With sulphuric acid it forms a blue solution, which, when heated or diluted, becomes yellowish-brown. It is decomposed by nitric acid. It is sparingly soluble in acetic acid. It dissolves in kreasote with a purple color, and on the addition of water is precipitated in crystals. It is insoluble in water, alcohol, ether, oil of turpentine, bisulphuret of carbon, and almond-oil. (BERZELIUS' *Jahrsbericht*, 1835, p. 408. THOMSON'S *Chem. of Organic Bodies*, 737.)

The above is an outline of the history of the products contained in



wood tar: when considered in reference to the various hydrocarbons already noticed as producible from coal-tar (p. 488, &c.), and by the destructive distillation of resins and oils, the whole subject acquires a considerable degree of interest, and leaves little doubt that the apparent complexity and incongruity which hangs over the inquiries as they now stand, will be done away by the further examination of their mutual relations, and by the attainment of more exact views of their ultimate and atomic constitution.

§ VI. AZOTIZED ORGANIC PRINCIPLES. PROTEINIFEROUS PRINCIPLES. ALBUMINE. GLUTINE. FIBRINE. CASEINE. EMULSINE. LEGUMINE. PROTEINE.

THE importance of starch, sugar, gum, and certain forms of lignine, as alimentary substances, will be evident from the preceding account of their sources and uses, but in consequence of the deficiency of *nitrogen* in those proximate principles, it is obvious that their nutritive powers must be limited, and that they cannot contribute to the reproduction of those parts of animals of which nitrogen is an essential element. Chemical physiologists, therefore, have divided the organic principles used as food, into two classes: the first containing the *non-azotized substances*, enumerated in the preceding sections; and the second, the *azotized principles* which we are about to examine. Under the notion that the former are chiefly concerned in sustaining the temperature of the body, by uniting with oxygen, and yielding the products which the blood disposes of in the lungs, under the form of carbonic acid and water, they have been termed *aliments of respiration*: oils and fats, afterwards to be noticed, are also aliments of respiration, and are common to animals and vegetables. The azotized substances, on the other hand, have been regarded as directly contributing to the formation of muscular fibre and other structures, and organs, and as supplying the leading principles of the blood; they have therefore been called *aliments of nutrition*. The full meaning of these terms will be more evident when the phenomena of respiration and secretion are more especially considered; I now advert to them as showing the importance of drawing a line of distinction between those proximate organic principles which do, and those which do not, contain nitrogen; and to the fact that, in reference to the two classes regarded as articles of food, the latter are exclusively of vegetable origin, with the exception, perhaps, of sugar, (which is an occasional product of disease in the human subject,) while the former are common both to vegetables and animals; but as they generally occur in comparatively small proportion in vegetables, whereas in animals they are abundant, they have often been especially designated *neutral animal principles*.

In consequence of the presence of *nitrogen* in these products, the results of their destructive distillation are characterized by the formation of carbonate of ammonia (p. 469), and other ammoniacal compounds; cyanogen, and some of its combinations, are also often produced (p. 737); and if we refer to the numerous compounds which may result in various ways, from the mutual agencies of carbon, hydrogen, oxygen, and nitrogen, we may at once form some notion of the extremely complicated results to which these decompositions may give rise. These products are also

in many instances associated with sulphur and with phosphorus, and the presence of these elements tends to additional perplexity, as regards the secondary compounds which heat and other agents give rise to, in their action upon them. Another consequence of their complex constitution is their tendency to what is termed *putrefaction*, by which, under the influence of air, moisture, and a due temperature, their component elements gradually tend to simpler forms of arrangement, giving rise, however, during the progress of the changes, to a great variety of intermediate, but very complicated products, associated with the development of animalcules, the formation of infectious and contagious matters, and of the various sickening odors belonging to what has been called *putrefactive fermentation*.

**I. ALBUMINE.** This term is applied to an organic principle, which is soluble in cold water, but when its solution is heated to about  $160^{\circ}$ , it becomes more or less opaque, and deposits white flakes, or if concentrated, forms a coagulum; and when thus coagulated, it remains insoluble\*. Albumine occurs in solution in the sap or juices of many vegetables, as of the potato, carrot, turnip, cabbage, asparagus, &c.; it is a constituent of the seeds of the cereal grasses, and of almonds, filberts, and most of the oily nuts; it abounds in the juice of the common houseleek. The properties of albumine are best studied in the white of egg (ovalbumine), or in the serum of the blood (seralbumine), so that we shall first consider its characters as derived from those sources, and afterwards advert to its existence in other animal and vegetable products, where it is found both in the liquid and solid state.

*The albumine of the white of egg* is contained in a delicate membranous texture, from which it may be separated by agitation or trituration with water, when the cellular membrane is gradually deposited, and the albumine remains mixed with the water: but it is difficult to obtain it in clear solution unless it be very dilute, in which case it passes the filter: a drop or two of solution of caustic potassa added to the white of egg dissolves the membrane, and then the solution may be more easily filtered. When carefully reduced to dryness by a gentle heat, or by evaporation in vacuo, ovalbumine is obtained in the form of a brittle transparent yellow substance, inodorous, insipid, and when triturated with cold water, resuming its original glairiness. When heated it exhales the usual products of azotized organic bodies, and a residue of carbon remains, which, in consequence of the phosphates which it contains, is very difficult of incineration; it leaves about 6 or 7 per cent. of saline matter, composed, according to Liebig, of carbonate, phosphate,

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\* The word is generally written *albumen*, especially as applied to the characteristic specimen of it in *white of egg*: I have adopted *albumine* as a generic term, assimilating with *fibrine*, *glutine*, *legumine*, *caseine*, &c., when similarly employed.

The term *albumen*, used by Pliny (*Hist. lib. xxviii. c. 4*) to denote the white of an egg, began, about the end of the last century, to be applied to certain organic substances, which have the property of coagulating when heated to about  $170^{\circ}$ .

In their natural state they are soluble in water, but lose this solubility by coagulation. The word *albumen* does not occur in the table of the New Chemical Nomenclature, published by the French chemists in 1787, but we find it employed by Fourcroy about the year 1789 (*Ann. de Ch. iii. 252.*) He and Vauquelin seem to have been the first chemists that attempted to fix its meaning with something like precision. (THOMSON, *Chemistry of Animal Bodies*, p. 180.)



and sulphate of soda, phosphate of lime, and chloride of sodium. Prout found traces of potassa and of magnesia in the white of egg, together with the preceding salts. Hatchett subjected 100 parts of dried white of egg to destructive distillation, and obtained carbonic acid, carburetted and sulphuretted hydrogen, hydrocyanic acid, carbonate of ammonia, a fetid oil, and 14.9 of spongy difficultly combustible charcoal, which by incineration, left 2.21 of ash, composed chiefly of carbonate and phosphate of soda, and phosphate of lime. The white of egg dried in vacuo, and digested in alcohol (sp. gr. 0.821) yields a solution containing soda, chloride of sodium, and fat; the residue in this case is no longer soluble in pure water, but forms with it a viscid mixture soluble in solutions of salts with alkaline bases. (LIEBIG.) 100 parts of the albumen of a newly-laid hen's egg, when carefully evaporated in vacuo, leave a residue = 15 parts; 100 parts of the coagulated white of a duck's egg (dried in vacuo over sulphuric acid) leave 13.65 parts of solid residue, which, steeped in water, acquires its original appearance, but in four days it only took up 68 of water, though it had lost 86.35. (CHEVREUL, *Ann. Ch. et Ph.*, xix. 46.)

*The albumine of the serum of blood* resembles that of white of egg, when similarly evaporated to dryness at a low temperature; but when reduced to powder, and digested in cold water, it is difficult of solution, unless a very small quantity of potassa or soda be added, or of a salt with an alkaline base, such as nitrate or sulphate of soda. As relates to all the ordinary properties of albumine, it may be considered as identical, whether from white of egg, or from serum, though as regards the action of certain reagents, there appear to be some slight differences between them. They are both slightly alkaline.

When a moderately strong aqueous solution of albumine, as it exists in the white of egg, or in serum, is heated to about 150° (145° to 148° DUMAS) it becomes opalescent, and at about 170° (166° DUMAS), it *coagulates*, becoming a white, translucent, and somewhat elastic substance, with which we are familiar in a hard-boiled egg; and when in this state it is cautiously dried, it no longer remains soluble in water, but becomes tough and horny; so that there is this characteristic distinction between albumine which has, and that which has not, undergone previous coagulation. As this coagulation ensues in close as well as in open vessels, it may be concluded that the proportion of water in the recent and in the concrete albumine is the same. 2 parts of white of egg and 1 of water entirely coagulate when duly heated, but equal parts remain, under the same circumstances, semifluid; a mixture of 1 part of white of egg and 10 of water becomes opaque, but is not coagulated; and a milkiness is perceptible when the white of egg forms only a thousandth part of the heated solution. (BOSTOCK, *Nicholson's Journ.*, xiv.; *Medico-Chirurgical Trans.*, I. & II.) When a new-laid egg, or one which has been greased or waxed upon the surface, is immersed in boiling water, the white does not so readily coagulate as in an old egg which has been simply exposed to air, a distinction, perhaps depending upon its having, in the latter case, lost a portion of water by evaporation through the shell, and being therefore in a somewhat less dilute state than in the fresh egg. According to Dumas, when dilute albumine is heated to 166°, it does not apparently coagulate, but it does so when

boiled; in this case the albumine, though heavier than water, gets blended with air and bubbles, and so forms a coagulated film or scum upon the surface; it is thus that the solid albumine forms a mobile filter which rises from all the points of the liquid to the surface, and is effectively used in the clarification of certain solutions. (*Chim. App. aux Arts*, VII. 454.) When coagulated albumine is continuously boiled in water for several hours, it shrinks up and becomes hardened, and, as it were, horny, communicating to the water traces of organic and saline matters. Heated in a copper digester with a little water up to the temperature of  $400^{\circ}$ , coagulated albumine almost entirely dissolves, blackening the interior of the vessel; the solution is brown, and has the odor of boiled meat (from the formation of osmazome?) (L. GMELIN.) Heated in a glass tube to about  $300^{\circ}$ , coagulated albumine forms a liquid which does not gelatinize on cooling, and which cannot again be coagulated. (WÖHLER.)

*Action of Acids on Albumine.* A clear aqueous solution of serum or of white of egg may be cautiously neutralized by the acids, without coagulation: on further dilution, the neutral liquor deposits a transparent gelatinous precipitate, which, when washed with distilled water, is free from acid and saline matters; it is soluble in acetic acid, in very weak alkalis, and in solutions of salts with alkaline bases, especially nitrate and sulphate of soda. According to Denis, this is pure albumine, and he ascribes the solubility of white of egg and of serum in water, to the presence of the free alkali and alkaline salts contained in those substances. The solution of this gelatinous albumine with nitre is coagulable by boiling.

When a solution of albumine, rendered neutral by the cautious addition of dilute sulphuric acid, is evaporated to dryness in vacuo, the yellow residue digested in water leaves a viscid substance containing sulphuric acid: the solution coagulates when heated to  $150^{\circ}$ , and is precipitated by alcohol, by excess of sulphuric acid, and by acetic acid, the resulting precipitate being a combination of albumine with sulphuric acid. This *sulphate of albumine* is always formed when albuminous solutions are precipitated by excess of sulphuric acid; it may be decomposed, and the acid abstracted, by carbonate of ammonia. (BERZELIUS.) When concentrated sulphuric acid is added to white of egg or serum, an immediate coagulation ensues, arising partly from the heat evolved. When sulphuric acid, diluted with from 2 to 4 parts of water, is added to a solution of albumine diluted with 1 or 2 parts of water, no immediate precipitate ensues, provided the liquors be cold, even on the addition of considerable excess of the acid; but after some hours a white flocculent precipitate falls which does not sensibly diminish in volume after repeated washings; hence, according to Hruschauer, the existence of a compound of albumine with sulphuric acid is questionable. (LIEBIG.) But even after continuous washing sulphuric acid may be detected in the coagulum.

Hydrochloric acid produces a coagulum in aqueous albuminous solutions when they are not very dilute, which is soluble in water, and again thrown down by the addition of an acid; it is also precipitated in a gelatinous form by a carbonate of ammonia. Albumine, like other proteine-compounds, dissolves when aided by heat, in concentrated hydro-



chloric acid, forming a blue or purple liquor; and when albumine has been thrown down by hydrochloric acid, it generally becomes reddish after washing and exposure to the air. This red or purple hue acquired by the action of hydrochloric acid is somewhat characteristic of all the varieties of albumine, and quill, horn, &c., exhibit it when heated in the acid; so also almonds, chestnuts, and other substances containing vegetable albumine, become similarly tinted.

Nitric acid precipitates albumine in aqueous solution, and after repeated washings the precipitate becomes viscid: upon the whole, nitric acid appears to be the most delicate of these tests of the presence of albumine, and to form a flocculent precipitate in solutions so dilute as not to be affected by the preceding acids. This precipitate is soluble in solution of ammonia, potassa, and soda. When coagulated white of egg is digested in very dilute nitric acid for some weeks, it acquires a yellow color, and is soluble in boiling water, the solution appearing to possess certain characters of gelatine, for it is precipitated by tannin and by hydrochlorate of tin. (HATCHETT, *Phil. Trans.*) Nitric acid of the sp. gr. 1.25 gradually tinges coagulated white of egg of a yellow color, dissolving a little of it, and forming malic acid, with the evolution of nitrogen: in 24 hours it falls into a pale yellow powder, which is acid, and contains nitrous and malic acid in combination with albumine. When thoroughly washed with water, it becomes more neutral, and of an orange color, still, however, reddening litmus and remaining insoluble in water, but soluble in caustic potassa. (BERZELIUS.) When coagulated white of egg is digested in hot nitric acid, nitrogen, nitrous gas, carbonic acid, and hydrocyanic acid are formed, and a dark-yellow solution is obtained, which is precipitated by the addition of water and of ammonia, and which contains malic acid, and bitter matter, and fat. (HATCHETT, *Phil. Trans.*, 1799.)

Phosphoric acid produces different effects on an aqueous solution of albumine, according to its state of hydration. The monohydrated acid throws it down abundantly in white flakes; the terhydrated acid, on the contrary, not only does not precipitate it, but redissolves the former precipitate.

Acetic acid occasions no precipitate in aqueous albumine even when heat is applied to the mixture; but if the acid be strong, and the albuminous solution not too dilute, a gelatinous compound appears, which is soluble in excess of the acid and in water. The acetic solution of albumine is precipitated by sulphuric, nitric, and hydrochloric acid, and by ferrocyanide of potassium. When it is evaporated to dryness, it leaves a transparent sour residue, soluble in warm water acidulated by acetic acid. (BERZELIUS.)

*Action of Alkalis upon Albumine.* Albumine is soluble in aqueous ammonia. When a concentrated aqueous solution of albumine is mixed with a strong solution of caustic potassa or soda, a gelatinous compound is the result, which is soluble in water, and if this aqueous solution be evaporated by a gentle heat, pellicles like those which form on boiled milk, gradually collect upon the surface. If the strong alkaline solution be boiled, ammonia is evolved, an alkaline sulphuret is produced which blackens the salts of lead, some phosphate of potassa is formed, and other changes ensue which have not been minutely investigated. A small piece of coagulated white of egg boiled with a diluted alkaline

solution of oxide of lead, or with acetate of lead supersaturated by potassa or soda, speedily blackens from evolved sulphur, and in this way sulphur may be detected in quill, wool, hair; in the almond, and many other vegetable substances; and, indeed, in all its organic compounds.

Lime, baryta, and strontia form insoluble combinations with albumine, which harden on drying. The compound obtained by mixing slaked lime with white of egg is sometimes used in the laboratory as a lute, spread upon strips of paper or linen; it is capable of resisting to a great extent the action of acid fumes. According to Bostock, a dilute solution of albumine (the white of one egg in a pint of water) is not precipitated by lime, baryta, or strontia water.

*Action of Salts upon Albumine.* These actions partly depend upon the presence of free alkali in the common varieties of albumine, and partly upon combinations which are formed between the albumine and the salts themselves, or their bases. Serum and the white of egg are coagulated by the greater number of the salts of the alkalis, earths, and oxides, and the precipitate usually contains both the acid and the base of the precipitant. The aqueous solutions of the salts of iron, copper, lead, mercury, and silver, yield precipitates which, when well washed, are compounds of albumine and the metallic oxide; but if the albumine be previously neutralized by acetic acid, no precipitate is occasioned by the salts of copper or of lead. The precipitate produced in the above cases is usually soluble in excess either of serum or white of egg, and also in solutions of the neutral salts of the alkalis, of iodide of potassium, phosphate of soda, ferrocyanide of potassium, and the dilute acids. (LIEBIG.)

Solutions of sulphate of iron and sulphate of copper give a precipitate even in very weak solutions of albumine, but it is easily redissolved as above stated. The subacetate of lead is a very perfect precipitant of all the forms of albumine: 1 part of fresh albumine of egg in 2000 of water, or 1 of dried albumine in 10,000 of water, is rendered turbid by this reagent. Corrosive sublimate is also a most delicate test of the presence of albumine; a four-hundredth part of liquid, and a two-thousandth of solid albumine, is precipitable by this test. (BOSTOCK.) The precipitate is blackened by potassa, and was consequently supposed to be a compound of hydrochlorate of albumine and calomel; but Lassaigne has shown (*Ann. Ch. et Ph.*, LXIV. 90), that it is soluble in alkalis and acids, and in solutions of alkaline chlorides, iodides, and bromides, and that it is a compound, apparently definite, of corrosive sublimate and albumine, in the proportion of 6·5 of the former to 93·5 of the latter; or, according to his equivalents, of 1 atom of bichloride and 10 atoms of albumine. The ready solubility of this compound in several saline and other liquids, may in many cases prevent the efficacy of the test; and when white of egg is used as an antidote to the poisonous effects of corrosive sublimate, chloride of sodium should be avoided, and vomiting excited as speedily as possible, in order to prevent the redissolution of the compound in the secretions of the stomach. Albumine is not precipitated by cyanide of mercury; it forms a yellow precipitate with chloride of gold which acquires a purple hue by exposure to light; chloride of platinum also forms with it a yellow coagulum.

On mixing the serum of the blood with small quantities of metallic



salts, and then adding a slight excess of caustic potassa, the oxides are not precipitated, but retained in soluble combination. The compound thus formed with peroxide of iron is pale yellow: that with protoxide of iron, green; with oxide of copper, blue; and colorless with oxides of mercury. When these solutions are heated, the albumine coagulates and carries the oxide with it. It is to this circumstance (says Dumas) that we are to ascribe the absorption of metallic salts or oxides by the intestines or the skin, which are thus carried into the serum of the blood to be eliminated with the excretions: it is thus, for example, that after the use of the preparations of mercury, oxide of mercury is found dissolved in the liquids of the body. These combinations are generally difficult of decomposition, and the metallic oxide can only be entirely separated by destroying the animal matter by heat. When excess of potassa is added to a mixture of albumine and hydrated oxide of copper, a transparent solution of a splendid violet color is obtained: it may be produced by adding the alkaline solution (either potassa or soda) to a mixture of serum and solution of sulphate or acetate of copper: it appears to be a peculiar double salt. If a dilute solution of sulphate of copper be dropped into a solution of albumine, a greenish-white precipitate is first formed, which redissolves on agitation, and is reproduced on a further addition of the precipitant, and even redissolved by great excess of it; it, however, reappears after some time, and is perfectly soluble in the acids: if, on the other hand, the albuminous solution be added to the sulphate of copper, the greenish precipitate first formed redissolves on agitation; but if after it has been reproduced, a great excess of the albumine be added, it is entirely redissolved. All these precipitates are soluble in potassa, forming intensely blue liquors: their composition has not been satisfactorily ascertained. (*Chim. App. aux Arts*, vii. 456.)

*Action of Organic Substances on Albumine.* Albuminous solutions are precipitated by *tannine*; the compound which is thrown down is of a pale brown or brownish-grey color when infusion of galls is used, and differs from tannogelatine in not being softened by heat. According to Mulder, this precipitate is a *tannate of proteine*. *Kreasote* forms a copious precipitate in solutions of albumine. They are not affected by those forms of rennet which copiously coagulate milk.

When ovalbumine or seralbumine is agitated with *alcohol*, a copious coagulum is produced, which is insoluble in water. *Ether* rather gelatinizes than coagulates the white of egg, when the two are shaken together; after a time a yellow liquor separates, which is not coagulated by heat, and a spongy albumine remains. When serum is similarly treated, no such precipitation ensues; the mixture separates into two portions, and the ether which floats upon the surface holds fat in solution. According to Alfred Taylor, ovalbumine and seralbumine are further distinguished as follows:—Add acetic acid to each, and boil; white of egg, if in sufficient quantity, coagulates, and remains coagulated at all temperatures; serum becomes opaline, and remains liquid, but it consolidates on cooling; this alternate liquefaction and coagulation by heat and cold may be indefinitely repeated.

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When an electric current is transmitted through liquid or aqueous albumine, the effects vary with the power used, and with the state of

dilution and purity of the albuminous liquor; the principal coagulation in these cases seems often to ensue at the negative electrode, especially in strong albuminous solutions; alkaline matter is there liberated, and a gelatinous compound produced, in which the bubbles of evolved gas become entangled: in other cases, the coagulation is most decided at the positive pole, where acid matter is set free. When small quantities of a saline albuminous liquor are operated upon with a comparatively high electric power, the heat evolved during the electro-chemical action is often sufficient to produce coagulation.

When white of egg or serum is left to itself at common temperatures, it gradually putrefies, and produces abundance of animalcules; but when rendered neutral, or only slightly acid, very different results ensue: in this case small spherical corpuscles are developed, which constitute the rudiments of a vegetable called *Penicilium glaucum*. The same changes ensue in various serous secretions, and in the serous part of pus; in short, every albuminous liquid rendered neutral by an acid, is subject to the same microscopic vegetation. For this purpose, very dilute sulphuric or acetic acid may be used; the liquid, at first transparent, becomes opalescent and turbid from the presence of minute particles in suspension; these gradually form a grey deposit, and the liquid resumes its transparency; but in about twelve hours a variable quantity of oval or circular vesicles may be discerned in it, which are perfectly independent of each other, and which, vegetating with various degrees of rapidity, obtain a perfect organization. (DUMAS.)

It has already been observed, that if fresh and uncoagulated albumine, as it exists in recent white of egg, or in serum, be evaporated in vacuo, or at a temperature not much exceeding  $100^{\circ}$ , it forms a yellow transparent substance, which redissolves in water, and retains its former characters; but if albumine has once been coagulated, its original properties cannot again be conferred upon it; for when the boiled white of egg, for instance, is dried, even at a low temperature, it acquires a horny appearance and is insoluble; so that *dry albumine* may be distinguished as *soluble* and *insoluble*. Its solubility has generally been referred to the presence of alkaline or other inorganic bodies; but Wurtz has shewn that it may be obtained pure, and yet soluble, by the following process. (*Ann. Ch. et Ph.*, October, 1844.) White of egg is diffused through twice its weight of water, and strained through linen to separate the membranes; subacetate of lead is then added, and the precipitate having been washed, is diffused through water, and subjected to a current of carbonic acid gas, by which the albuminate of lead is decomposed, carbonate of lead being formed, and the albumine retained in solution by the water; this solution, when filtered, still retains traces of lead, which may be removed by adding a few drops of an aqueous solution of sulphuretted hydrogen, and carefully heating to  $140^{\circ}$ , till the liquor just becomes turbid, after which it is again filtered and evaporated in a shallow capsule at a temperature of  $120^{\circ}$ . The residue is pure soluble albumine, transparent, almost colorless, neutral, and containing no trace of carbonate of soda, and scarcely a trace of phosphate of lime: it is almost entirely soluble in warm water, and has a very slight acid reaction on litmus; it coagulates at  $140^{\circ}$  to  $150^{\circ}$ . Alcohol, the concentrated acids, solution of bichromate of potassa, of alum, of corrosive



sublimate, and of subacetate of lead, produce precipitates in its aqueous solution similar to those with white of egg. Its ultimate composition is the same as that of insoluble albumine. The compound of seralbumine with oxide of lead is not so completely decomposed by carbonic acid, as that of ovalbumine.

The ultimate cause of the *coagulation of albumine*, and the nature of the changes which it undergoes in that operation, have not been ascertained. “It is,” says Dumas, “probably a simple isomeric modification of this body, analogous to that by which cyanic acid is converted into cyanuric acid; so that it would be interesting to endeavour to ascertain whether the atomic weight of coagulated albumine is not double or triple that which belongs to liquid albumine.”

We have many ultimate analyses of albumine, all tending to the conclusion, that when free from foreign matters, its composition is identical, whatever may be its source. The following are some of these results :—

|               | Dumas and Cahours.                          |     |        |     |        | Jones.      | Scherer.                                    |     |         |     |         |
|---------------|---|-----|--------|-----|--------|-------------|---|-----|---------|-----|---------|
|               | <i>Serum of Blood. White of Egg. Wheat.</i> |     |        |     |        | <i>Rye.</i> | <i>Fluid of hydrocele. Fluid of dropsy.</i> |     |         |     |         |
| Carbon .....  | 53·32                                       | ... | 53·37  | ... | 53·74  | ...         | 54·75                                       | ... | 54·921  | ... | 54·302  |
| Hydrogen .... | 7·29  | ... | 7·10   | ... | 7·11   | ...         | 7·77  | ... | 7·077   | ... | 7·176   |
| Oxygen, &c.   | 23·69                                       | ... | 23·76  | ... | 23·50  | ...         | 21·65                                       | ... | 22·537  | ... | 22·805  |
| Nitrogen..... | 15·70                                       | ... | 15·77  | ... | 15·66  | ...         | 15·83                                       | ... | 15·465  | ... | 15·717  |
| Albumine .... | 100·00                                      |     | 100·00 |     | 100·00 |             | 100·00                                      |     | 100·000 |     | 100·000 |

In these analyses the proportion of sulphur and phosphorus is not separately specified, but included with the oxygen. Mulder has separately estimated these elements; the following are his analyses of the albumine of serum and of egg.

|                  | Seralbumine. | Ovalbumine. |
|------------------|--------------|-------------|
| Carbon.....      | 54·84        | 54·82       |
| Hydrogen .....   | 7·09         | 7·11        |
| Oxygen .....     | 21·23        | 21·30       |
| Nitrogen .....   | 15·83        | 15·94       |
| Sulphur .....    | 0·68         | 0·38        |
| Phosphorus ..... | 0·33         | 0·45        |
| Albumine .....   | 100·00       | 100·00      |

II. GLUTINE. The term *gluten* was originally applied to the grey, viscid, tenacious, and elastic matter which is obtained by subjecting wheaten flour to the continuous action of a current of water. The best mode of proceeding is to tie up the flour in a coarse cloth, and knead it under a stream of water till the starch and soluble matters (consisting chiefly of albumine, gum, and sugar,) are washed out, and till the water runs off clear and colorless. The residuary gluten consists chiefly of four distinct substances, which may be separated as follows. (DUMAS and CAHOURS, *Ann. Ch. et Ph.*, 1842, vi. 389.) It is boiled in alcohol, strong at first, and afterwards weaker; there remains a grey fibrous substance, (*vegetable fibrine*,) and the alcoholic solution deposits *caseine* as it cools; if after this it be poured off and carefully evaporated, a pultaceous substance is obtained, which is glutine mixed with more or less fat; to free it from the latter, it is dried, pulverised, and digested in anhydrous ether as long as it imparts anything to that solvent; the residue is then washed with alcohol, afterwards with water, and ultimately dried. It appears,

therefore, that the crude or original gluten is a mixture of fibrine and caseine, with *glutine*, and a peculiar oily or fatty matter. Glutine is especially abundant in wheat, to the flour of which it gives its peculiar tenacity when formed into dough; it also occurs in the other cereals, and is probably commonly associated with albumine and caseine in vegetables.

Glutine has been analysed by Marcet, (*Mem. Soc. Ph., &c. de Genev.*, iii. 217,) Jones, (*Ann. der Chem. und Pharm.*, XL. 66,) Boussingault, (*Ann. Ch. et Ph.*, LXIII. 229,) and Dumas and Cahours, (*Ann. Ch. et Ph.*, 1842, vi. 419;) and, as Marcet first observed, the results show that, as far as the relative proportions of its ultimate elements are concerned, it is almost identical with albumine; so that it may be considered as isomeric with that principle: it also contains sulphur and phosphorus, but these have not as yet been quantitatively determined, and are included with the oxygen in the following tables.

|                         | Marcet. | Jones. | Boussingault. | Dumas and<br>Cahours. |
|-------------------------|---------|--------|---------------|-----------------------|
| Carbon .....            | 55·7    | 55·22  | 53·75         | 53·27                 |
| Hydrogen.....           | 7·8     | 7·42   | 7·55          | 7·17                  |
| Oxygen, &c.....         | 22·0    | 21·38  | 24·20         | 23·62                 |
| Nitrogen .....          | 14·5    | 15·98  | 14·50         | 15·94                 |
| Xanthoproteic acid..... | 100·0   | 100·00 | 100·00        | 100·00                |

The general chemical characters of glutine have been but imperfectly ascertained; the mode of separating it from crude gluten shows its solubility in cold alcohol: it is soluble in acetic and in hydrochloric acid, and the latter solution has the characteristic violet tint of the bodies of this class. It appears to be the substance long ago described by Taddei under the name of *gliadine*, (from *γλια*, *glue*,) and the principle which he called *zimome*, (from *ζυμη*, *leaven*, or *ferment*,) was apparently vegetable albumine. Glutine is exclusively a vegetable product.

III. FIBRINE. Under this name a principle has been described common to animals and vegetables, but the term *fibrine* was originally applied to this substance as derived from the blood. It is easily obtained by agitating blood, as it flows from the vessels, with a rod, to the twigs of which it adheres in the form of fibrous filaments, which may be cleansed of coloring and other soluble matters, by repeated washings in fresh portions of water. Fibrine may also be obtained from the clot of coagulated blood, by tying it up in a piece of linen and kneading it in running water till it remains colorless; or by subjecting slices of the coagulum, placed upon a sieve, to the continuous action of a stream of water; but the first is the best process.

In its humid state, fibrine retains about 75 *per cent.* of water: it requires to be further purified by digestion in boiling alcohol or ether, by which a portion of fatty matter is removed, and it may then be dried at a temperature not exceeding 240°. It is insipid and inodorous, of a yellowish-grey tint, translucent, and hard and horny. Fibrine may also be obtained from muscle. A quantity of lean beef was cut into small pieces and macerated in water for fifteen days, changing the water every day, and at the same time subjecting the beef to pressure. The shreds of muscle were then boiled repeatedly in fresh portions of water, and ultimately pressed and dried. (HATCHETT, *Phil. Trans.*, 1800, p. 327.)



Immersed in water, dry fibrine absorbs about thrice its weight, and regains much of its original appearance before having been dried. It is insoluble in cold and in hot water, but when subjected to protracted ebullition, it shrinks, and becomes friable, traces of ammonia are evolved, and a liquor is obtained which, when filtered and evaporated, leaves a brittle yellowish substance, having the smell of boiled meat, and soluble in water; it does not gelatinize, but it yields a peculiar flocculent precipitate with infusion of galls. The residuary insoluble portion of the fibrine has lost the original properties of that substance, and has acquired those of coagulated albumine. Dumas observes that this experiment establishes a well-marked line of demarcation between fibrine and albumine, or caseine, which two last substances do not yield these products of fibrine.

When fibrine is covered with water, it becomes in a few days viscid, and acquires the odor of old cheese; it produces ammoniacal salts, and then the mixture gradually liquefies; in this state it coagulates by heat, and by the addition of alcohol and of solution of corrosive sublimate, resembling, in those respects, serum. It has sometimes been supposed that, under the joint influence of air and moisture, fibrine is convertible into fat; but the experiments of Gay-Lussac and Chevreul have shown that, when fibrine is pure, there is no fatty residue: 100 grains of pure fibrine were kept covered with water in a filter, and, after some months, the whole gradually disappeared, leaving only traces of a brown matter upon the paper. A piece of the muscle of beef, and a slice of liver treated in the same way, left the fat which they had originally contained, upon the filter; so that, in cases where accumulations of fatty matter (adipocere) have been found as the result of the decomposition of flesh, they are to be referred to the fat originally contained in the textures, which has resisted decomposition, whilst the fibrinous parts have gradually dissolved away. (*Ann. Ch. et Ph.*, 1817, iv. 71.)

Fibrine is not altered by heat, till it begins to decompose; it then fuses, swells up, and burns with a yellow sooty flame, leaving a porous and brilliant charcoal, which is difficult of incineration; the ash amounts to about 0·8, or 1 *per cent.* of the weight of the dry fibrine; it is neither acid nor alkaline, and consists chiefly of phosphate of lime, with a little phosphate of magnesia and traces of silica and generally of iron, but perfectly pure fibrine affords no trace of the latter metal.

Sulphuric acid changes dry fibrine into a yellow gelatinous mass, insoluble in excess of the acid; but if large quantities be operated on, heat is evolved, and in that case the mass blackens, and sulphurous acid is evolved. When fresh fibrine is immersed in sulphuric acid diluted with five or six parts of water, it shrinks, and a compound of the acid with fibrine is formed. Dilute sulphurous acid does not dissolve fibrine, but when digested with it, retains a substance in solution, which, after the saturation of the acid, is precipitated by tincture of galls, but not by alkalis nor by ferrocyanide of potassium. It would seem, therefore, that the acid retains a substance analogous to that which is produced by boiling fibrine in water. The shrunk sulphate of fibrine above adverted to, when washed with water, gradually becomes a transparent jelly soluble in pure water, from which, however, it is again precipitated by dilute sulphuric acid. (DUMAS.)

When fibrine is digested in nitric acid nitrogen is evolved, and a peculiar yellow substance, first examined by Fourcroy and more recently by Mulder, (*Ann. der Pharm.*, xxvii. 78,) is formed, which, when purified by boiling it in water and then in alcohol, has been termed *Xanthoproteic acid*; it is friable, inodorous, and tasteless, but reddens moistened litmus paper; it is very sparingly soluble in boiling water, which deposits it on cooling; it forms soluble compounds with the alkalis, of a deep orange color, from which the acids throw it down unchanged; it is decomposed by continued ebullition with excess of potassa; subjected to destructive distillation it yields a fetid oil and ammoniacal products, and leaves an easily incinerable coal. According to Mulder, the elements of xanthoproteic acid are,

|                         |        |
|-------------------------|--------|
| Carbon.....             | 51·65  |
| Hydrogen .....          | 6·45   |
| Oxygen .....            | 27·83  |
| Nitrogen .....          | 14·07  |
| <hr/>                   |        |
| Xanthoproteic acid..... | 100·00 |

From his analysis of the *Xanthoproteate of lead* he derived the formula  $C_{34}H_{24}O_{12}N_4, PbO$ , and he regards the free acid as containing 2 atoms of water, its ultimate composition being  $C_{34}H_{26}O_{14}N_4$ . The neutral *Xanthoproteates* are orange-yellow, while those with excess of acid are more or less red; they are not crystallizable; those which are soluble are formed by the direct union of the acid and base; the others, by double decomposition. The product of the action of nitric acid on albumine, adverted to in a preceding paragraph, (p. 1222), is also probably xanthoproteic acid.

Hydrochloric acid at first gelatinises fibrine, and afterwards forms with it a deep blue liquor, which, on dilution with water, lets fall a white hydrochlorate of fibrine. The action of very dilute hydrochloric acid upon fibrine has been studied by Bouchardat and Sandras, (*Ann. Ch. et Ph.*, Août, 1842.) They found that the fibrine of blood and of muscle, when immersed in 10 times its weight of water so slightly acidulated by hydrochloric acid as scarcely to be perceptibly sour, (about 10 drops of the acid to a quart of water) became swollen and gelatinous in about twelve hours at common temperatures; and that this jelly triturated with water and filtered, yielded a solution, which coagulated by heat, gave a precipitate with ferrocyanide of potassium, and what appeared paradoxical, it afforded a precipitate on the addition of hydrochloric acid, not soluble except in excess of that acid. The bearing of these facts upon the theory of *digestion* will be afterwards noticed. According to Dumas and Cahours, water holding a millionth part of hydrochloric or hydrobromic acid, has the property of gelatinising, though not of dissolving fibrine, even when the latter was dry, or had been for some time in contact with alcohol: but the addition, under these circumstances, of a few drops of gastric juice, especially when aided by a temperature of  $95^{\circ}$  or  $96^{\circ}$ , caused the entire solution of the fibrine in a couple of hours. Runnet produced the same effect.

Phosphoric acid with 1 atom of water, acts upon fibrine in the same way as sulphuric acid. The acid with 3 atoms of water converts fibrine



into a gelatinous mass, which is soluble in water, and the solution is not affected by excess of the acid.

Fibrine is rapidly penetrated by concentrated acetic acid, and is converted by it into a colorless jelly soluble in hot water. When this solution is gently evaporated it becomes covered by a pellicle, and assumes a gelatinous form, which on drying, loses the greater part of the acetic acid, and the fibrine remains, opaque, and insoluble in cold and hot water. When another acid is added to the acetic solution of fibrine, a precipitate is formed composed of fibrine and the added acid. On the addition of an alkali the fibrine is at first precipitated, but it is soluble in excess of the alkali. The fibrine of young animals is more easily acted on by acetic acid than that of old ones, so that there is in this respect a material difference between the fibrine of veal and of beef. (DUMAS.)

Fibrine is soluble in weak solutions of caustic potassa and soda, first becoming gelatinous, and then slowly forming a yellowish solution, especially if raised to a temperature of  $120^{\circ}$  to  $130^{\circ}$ ; it is slightly turbid, but becomes clear when filtered; it blackens silver, and exhales the odor of sulphuretted hydrogen on the addition of an acid. According to Berzelius (*Lehrbuch*), a neutral compound of fibrine and potassa may be obtained by adding acetic acid to the dilute alkaline solution, till the fibrine begins to be thrown down, and filtering. This liquor has some of the properties of liquid albumine, and when evaporated, yields a yellow transparent residue, which first gelatinises in warm water, and then forms a solution which is precipitated by the acids: the precipitate with acetic acid redissolves in excess of that acid, and in terhydrated phosphoric acid, and has the general characters of the original fibrine.

When fibrine is gently heated in a concentrated solution of caustic potassa, a little ammonia is disengaged, and a compound of proteine and potassa is retained in solution, from which the acids throw down proteine, which is neither gelatinisable nor soluble in acetic acid.

Caustic ammonia seems to act upon fibrine in the same way as the fixed alkalis, but its action is much less energetic.

Both the ferrocyanic and the ferridcyanic acid combine with fibrine; the compounds are obtained in the form of white and yellow precipitates, by adding solutions of ferrocyanide and ferridcyanide of potassium to the acetic solution of fibrine. The white precipitate is insoluble in the dilute acids, but the alkalis decompose it, and forming ferrocyanides, separate the fibrine in its gelatinous and soluble form. The yellow precipitate (obtained by the ferridcyanide,) is much more soluble than the preceding. According to Denis, (*Sur le Sang, et les matières albumineuses*, Paris, 1838, 1842,) when fibrine is dissolved in water holding certain neutral salts in solution, a liquor may be produced having the properties of liquid albumine; but, in this case, the fibrine must be obtained by the spontaneous coagulation of venous blood, which, cut into slices and washed, dissolves readily in certain saline liquors, which scarcely act upon the fibrine of arterial blood, or upon that which has been obtained by agitation. 150 parts of this *venous fibrine*, digested in a solution of 50 parts of nitre and 3 of soda in 300 of water, at a temperature of about  $100^{\circ}$ , yields a liquor which is coagulable by heat in the manner of liquid albumine.

The alkaline solution of fibrine yields precipitates with several of the

metallic salts, which are compounds of fibrine with the respective metallic oxides, and some of which are entirely soluble in caustic potassa. When digested in solutions of sulphate of iron, sulphate of copper, or chloride of mercury, fibrine combines with those salts, shrinks up, and loses all tendency to putrefaction.

Both the alkaline and the acid solutions of fibrine are precipitated by tannine, and a tannate of fibrine is thrown down. When humid fibrine is immersed in solution of tannine and afterwards dried, it becomes tough and hard, and resists putrefaction.

*Vegetable Fibrine.* When the crude gluten of wheat (p. 1226), after having been purified by abundant washing in water, is boiled first in strong and then in weaker alcohol, there remains a grey fibrous residue, which Dumas has designated *vegetable fibrine*, (*Ann. Ch. et Ph.*, 1842, vi. 389, 400): this is the *vegetable albumine* (Pflanzeneiweiss) of Berzelius, and according to Mulder and Liebig, fibrine and albumine are identical as to ultimate composition; whereas Dumas and Cahours, who took many precautions in the purification of the vegetable fibrine which they analyzed, found rather more nitrogen and less carbon in fibrine; the latter chemists appear to limit the term “vegetable albumine” to that substance as it is contained in the washings of wheat flour, and in the expressed sap or juices of certain vegetables, which are rendered turbid, or coagulated by heat.

The ultimate composition of fibrine from various sources has been determined by Jones, by Scherer, and by Mulder (*Ann. der Pharm.*, xlv. and xlviii.), and by Dumas and Cahours, with the following results, the sulphur, amounting according to Mulder to 0·36 *per cent.*, and the phosphorus to 0·33 *per cent.*, being included within the oxygen.

|                  | A.          | B.           | C.           | D.                    | E.           | F.           | G.           |
|------------------|-------------|--------------|--------------|-----------------------|--------------|--------------|--------------|
|                  | Scherer.    | Jones.       | Mulder.      | Dumas and<br>Cahours. | Do.          | Do.          | Do.          |
| Carbon .....     | 54·1        | 53·83        | 54·56        | 52·78                 | 52·77        | 52·57        | 53·23        |
| Hydrogen .....   | 7·3         | 7·02         | 6·90         | 6·96                  | 6·95         | 7·07         | 7·01         |
| Oxygen, &c. .... | 22·9        | 23·56        | 22·82        | 23·48                 | 23·77        | 23·81        | 23·35        |
| Nitrogen .....   | 15·7        | 15·58        | 15·72        | 16·78                 | 16·51        | 16·55        | 16·41        |
|                  | <hr/> 100·0 | <hr/> 100·00 | <hr/> 100·00 | <hr/> 100·00          | <hr/> 100·00 | <hr/> 100·00 | <hr/> 100·00 |

A and B, vegetable fibrine; C, fibrine of venous blood; D, fibrine of human blood; E, fibrine of the blood of a dog fed for ten weeks upon meat; F, fibrine of the blood of a dog fed for ten weeks upon bread; G, fibrine of wheaten flour.

IV. CASEINE. This term has been chiefly applied to the peculiar coagulable principle of milk. A similar substance is occasionally found in the blood, in the pancreatic juice of the ox and sheep, (L. GMELIN, *Handbuch*,) and in pus; it occurs also in vegetables.

Several complicated processes have been suggested by Berzelius, Rochleder, and others, for the preparation of pure caseine, but none of them afford very satisfactory results. It may be procured nearly pure, by coagulating well-skimmed milk heated up to 150° or 160°, by a few drops of acetic acid; the curd so obtained is spread upon a linen strainer and thoroughly washed with water; it is then pressed dry, and digested first in boiling alcohol, and then in ether, and carefully dried. It should



then be pulverised, and again digested in ether till perfectly free from all traces of grease, and lastly dried at  $240^{\circ}$  or  $250^{\circ}$ .

Caseine thus prepared is a white, opaque, and hard substance, insipid and inodorous, and insoluble in water; even when boiled for several hours in water, scarcely an appreciable portion is taken up. When caseine is precipitated by an acid from its solution in alkali, or by an alkali from its solution in an acid, it always retains the property of reddening litmus, even after having been dried at  $300^{\circ}$ , but it does not communicate any acidity to water in which it is boiled, nor does it expel carbonic acid from bicarbonate of soda at common temperatures. (DUMAS.)

Caseine has a strong tendency to combine both with acids and with bases, and the contradictory accounts of its properties seem in great measure to have arisen from its not having been examined in a state of purity. What has been termed *soluble caseine* by Berzelius and Braconnot appears to be a compound of caseine with potassa. When an acid is added to an alkaline solution of caseine, the precipitate which falls is a more or less pure caseine combined with phosphate of lime, which, however, may be abstracted by excess of the acid. If excess of acid be used in forming this precipitate, a compound of the acid with caseine falls. When acetic, oxalic, or tartaric acid are employed, the precipitate is soluble in excess of those acids, but hydrochloric and sulphuric acids form precipitates in these solutions. The compounds of caseine with the mineral acids are soluble in pure water and in alcohol.

When caseine is precipitated by sulphuric acid, the precipitate (sulphate of caseine) may be re-dissolved by the addition of slight excess of carbonate of potassa; the solution is turbid, but gradually becomes clear after having been mixed with alcohol. When this solution is evaporated, a white pellicle similar to that which appears upon boiled milk, is produced, and a substance ultimately remains, resembling gum arabic, which is soluble in hot and cold water. The alkaline solution is not precipitated by phosphoric acid: it is precipitated by solution of alum, chloride of tin, acetate of lead, protosulphate of iron, sulphate of copper, corrosive sublimate, and the nitrates of mercury and silver. Ferrocyanide of potassium acts upon the compounds of caseine similarly to those of albumine.

According to Mulder, the precipitates which are formed by adding the acids to milk are not permanent compounds of caseine and the respective acids, inasmuch as the whole of the acid may be removed by continuously washing the coagulum in water.

When caseine precipitated by acetic acid is kept under water in a covered vessel, it first becomes sour, and then evolves ammonia, and acquires the odor of old cheese. The phenomena of the putrefaction of cheese have been studied by Proust (*Ann. Ch. et Ph.*, x. 29,) and by Braconnot (*Ann. Ch. et Ph.*, xliii. 337): these will be afterwards adverted to.

*Vegetable caseine* was obtained from the crude gluten of wheat by Dumas and Cahours, by boiling it in weak alcohol; the solution so obtained deposited flakes of caseine on cooling; it was purified by washing first in water, and then in alcohol and ether: its properties corresponded with those of the caseine of milk. (*Ann. Ch. et Ph.*, 1842, vi. 417.)

Caseine is distinguished from albumine by its not coagulating when heated in dilute solution, and by being precipitated from such solution by acetic acid. The coagulability by rennet, as in the process of curd and cheesemaking, is also one of its distinctive characteristics. It contains sulphur, to the amount of 0·36 *per cent.* (MULDER), but no phosphorus, not at least in the peculiar state of combination in which that substance (and sulphur) is found in albumine and fibrine; but it is intimately combined with a certain proportion of phosphate of lime.

The ultimate composition of caseine has been determined by several chemists; it is considered by Dumas and Cahours as identical with albumine. The following are some of these results taken from the sources already quoted. (See also LIEBIG, *Chim. Organique*, iii. 259.)

|               | From Cow's Milk. |      |              |      |                    |      | Wheat.             |      | Vegetable Caseine. |      |              |
|---------------|------------------|------|--------------|------|--------------------|------|--------------------|------|--------------------|------|--------------|
|               | Scherer.         |      | Mulder.      |      | Dumas and Cahours. |      | Dumas and Cahours. |      | Scherer.           |      | Jones.       |
| Carbon .....  | 54·67            | .... | 54·96        | .... | 53·50              | .... | 53·46              | .... | 54·14              | .... | 55·05        |
| Hydrogen ...  | 7·30             | .... | 7·15         | .... | 7·05               | .... | 7·13               | .... | 7·16               | .... | 7·59         |
| Oxygen, &c.   | 22·35            | .... | 22·09        | .... | 23·68              | .... | 23·37              | .... | 22·03              | .... | 21·47        |
| Nitrogen .... | 15·68            | .... | 15·80        | .... | 15·77              | .... | 16·04              | .... | 15·67              | .... | 15·89        |
|               | <hr/> 100·00     |      | <hr/> 100·00 |      | <hr/> 100·00       |      | <hr/> 100·00       |      | <hr/> 100·00       |      | <hr/> 100·00 |

V. EMULSINE. *Amandine. Synaptase.* These terms have been applied to an albuminoid principle contained in certain oleaginous seeds and kernels, and more especially in *almonds*, from which it is most easily obtained. Dumas and Cahours, in their valuable memoir "On the Neutral and Azotized Products of Organization" (*Ann. Ch. et Ph.*, 1842, vi. 385), consider emulsine and legumine as identical, and the result of their ultimate analysis seems to justify such a conclusion; so also legumine and caseine are regarded by Liebig as one and the same principle; but though it will presently be seen that, as far as concerns the quantitative proportions of the carbon, hydrogen, oxygen, and nitrogen contained in the substances now under consideration, they may all be regarded as derived from one radical, yet there are peculiarities belonging to each sufficient to characterize them as distinct, or perhaps isomeric proximate principles.

Emulsine may be obtained, according to Dumas and Cahours, by macerating the almond cake which remains after the oil has been expressed, in cold water, for a few hours, and filtering the liquor; the clear solution affords a precipitate of emulsine on the careful addition of acetic acid; to render it perfectly pure, it should be washed in water and then with alcohol, dried, pulverized, digested in ether, and finally dried in vacuo at 285°.

When emulsine is thrown down by weak acetic acid from its concentrated aqueous solution, it always falls in the form of a white nacreous precipitate; but if the solution be very dilute, it forms a flocculent deposit. It is insoluble in boiling water, in cold alcohol and ether, and in weak alcohol at its boiling point. Cold water, on the other hand, dissolves it abundantly, and this solution affords a coherent flocculent precipitate when boiled, much resembling coagulated albumine. It follows, therefore, that if we heat an aqueous solution containing emulsine and albumine, both these substances will be coagulated.



Robiquet obtains pure emulsine as follows. Sweet almonds are pulverized and subjected to pressure without heat, to separate as much of the fixed oil as possible; the residuary cake is then macerated for two hours in twice its weight of cold water, and the liquid expressed and filtered. The liquor is freed from albumine, legumine, and gum, by the addition of acetic acid and acetate of lead, and being filtered from the lead precipitate, the filtrate is deprived of lead by sulphuretted hydrogen, the excess of which is removed by exposure in vacuo. Alcohol is then added, which throws down emulsine, and retains sugar in solution. (*Journ. de Pharm.*, 1838, p. 328.)

Richardson obtained emulsine by mixing emulsion of sweet almonds with four times its volume of ether; the mixture was well agitated, and then left at rest for some days: a clear liquid gradually separated, on which the ether and a quantity of insoluble matter floated. The clear aqueous liquor being drawn off, was mixed with alcohol, when an abundant white precipitate of emulsine was obtained, which was thoroughly washed and then perfectly dried in vacuo over sulphuric acid. (THOMSON'S *Organic Chemistry*, 1838, p. 683.)

Dumas assigns the following properties to emulsine. It is soluble in cold, but insoluble in hot water; so that when a mixed solution of albumine and emulsine is heated, the resulting coagulum contains both those substances. In concentrated acetic acid, emulsine swells up, becoming gelatinous and soluble in hot water, from which it may be obtained by evaporation in a gummy form, soluble in water, and not changed in composition. When dilute acetic acid is added to a solution of emulsine, it is at first precipitated, but an excess of the acid entirely redissolves the precipitate, forming a clear solution from which ammonia throws down the emulsine, and excess of ammonia again dissolves it. Dilute hydrochloric acid precipitates the emulsine in the same way as the acetic acid; concentrated hydrochloric acid redissolves the precipitate, forming a deep blue liquor, similar to that produced by albuminous substances. Sulphuric acid throws down emulsine from its aqueous solution; but if dry emulsine be triturated with concentrated sulphuric acid, a brown solution is formed. Dilute nitric acid precipitates emulsine with the same appearances as the preceding acids; but the concentrated acid dissolves it with the evolution of nitrous gas. Terhydrated phosphoric acid (which does not precipitate albuminous solutions) occasions a precipitate in the solution of emulsine.

Emulsine is soluble in cold solutions of potassa, soda, and ammonia; when heated with either of the two former alkalis, ammonia is disengaged, and sulphuretted hydrogen becomes manifest. When emulsine is heated with lime or baryta, and water, there is also a disengagement of ammonia, and soluble compounds are formed with those bases, seeming to indicate the production of a peculiar acid.

Emulsine is coagulated by runnet, but not until after some hours, when it is entirely thrown down in a pure state, and the remaining liquor affords no precipitate on the careful addition of dilute acetic acid.

Emulsine, having all the characters of that from almonds or nuts, may also be obtained from white mustard seed, the powder of which, macerated for a few hours in cold water, gives a solution precipitable by acetic acid.

The term *Synaptase* has been applied to emulsine by Robiquet (from *συναπτω*, *adsum*) in consequence of its necessary *presence* in the conversion of amygdaline into hydrocyanic acid and hydruret of benzoyle. (See *Amygdaline*.) That emulsine contains sulphur is shewn by the blackening of almonds and other substances which yield it, when boiled in an alkaline solution of oxide of lead, but its relative proportion has not been determined, and in the following analyses it is included with the oxygen:—

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|                  |              | Dumas and Cahours.         |              |                   |                                 |       |              |
|------------------|--------------|----------------------------|--------------|-------------------|---------------------------------|-------|--------------|
|                  | Richardson.  | <i>From sweet Almonds.</i> |              | <i>From Nuts.</i> | <i>From white Mustard-seed.</i> |       |              |
| Carbon .....     | 48·81        | .....                      | 50·90        | .....             | 50·73                           | ..... | 50·83        |
| Hydrogen .....   | 7·79         | .....                      | 6·76         | .....             | 6·95                            | ..... | 6·72         |
| Oxygen, &c. .... | 24·41        | .....                      | 23·41        | .....             | 23·56                           | ..... | 23·87        |
| Nitrogen .....   | 18·99        | .....                      | 18·93        | .....             | 18·76                           | ..... | 18·58        |
|                  | <hr/> 100·00 |                            | <hr/> 100·00 |                   | <hr/> 100·00                    |       | <hr/> 100·00 |

VI. LEGUMINE is the azotised principle of peas, beans, and many similar seeds; it is considered as identical with caseine by Liebig and Wöhler, (LIEBIG, *Chim. Organ.*, iii. 220,) and with emulsine by Dumas and Cahours (*Ann. Ch. et Ph.*, 1842). It may be best obtained by steeping ground peas in warm water for a few hours, so as to soften them, and then macerating them in cold water for about an hour, and pressing out the liquor, which is left to deposit its suspended starch, and filtered. Acetic acid diluted with 8 or 10 parts of water is then carefully dropped into the filtrate so as to precipitate the legumine, avoiding excess of the acid, which would redissolve the precipitate. It falls in the form of white flakes, and after having been washed on a filter is to be dried, pulverized, and freed from adhering fat by digestion in ether. Legumine may be obtained from lentils with the same facility as from peas, but it is less easily procured from beans (*haricots*), in consequence of their containing a gummy matter which interferes with its precipitation and with the filtration of the liquors.

The properties ascribed to legumine by Braconnot are as follow: when heated with a vegetable acid, oxalic or citric acid for example, it yields a mucilaginous solution, in which nitric, sulphuric, hydrochloric, and phosphoric acids give a white precipitate; it is also precipitated by infusion of galls, by the nitrates of baryta and lead, by chloride of calcium, by sulphate of copper and sulphate of iron, and by the greater number of the metallic salts with mineral acids; it is not precipitated by the acetates of lead, baryta, or alumina, nor by solution of corrosive sublimate. It is soluble, both in its pure state and when combined with mineral acids, in weak alkaline solutions and in their carbonates, as in carbonates of potassa, soda, and ammonia. When boiled in a concentrated solution of caustic potassa or soda, ammonia is given off, and dilute sulphuric acid evolves sulphuretted hydrogen when added to these alkaline solutions: with lime and baryta it forms insoluble combinations. Alcohol and the mineral acids throw it down from its solution in the alkalis.

Liebig supposes that grape juice, and other vegetable juices which are deficient in albumen, derive their fermentative power from soluble legumine; it is very soluble in tartaric acid, and to its presence he ascribes the tendency of sugar to form alcohol and carbonic acid, instead



of mucilage and lactic acid. Dumas and Cahours remark that the seeds which derive their principal nutritive power from legumine are more effective as aliments when boiled, than when in their ordinary state, whence they conclude that coagulated legumine is more nutritious than when it is in its soluble form.

Legumine has been analyzed by Dumas and Cahours, by Varrentrapp and Will, and by Rochleder, with the following somewhat discordant results:—

|                | Dumas and Cahours. |                    |                      | Rochleder.         |                   | Varrentrapp and Will. |
|----------------|--------------------|--------------------|----------------------|--------------------|-------------------|-----------------------|
|                | <i>From Peas.</i>  | <i>From Beans.</i> | <i>From Lentils.</i> | <i>From Beans.</i> | <i>From Peas.</i> | <i>From Peas.</i>     |
| Carbon.....    | 50.53              | 50.46              | 50.69                | 51.15              | 54.49             | 51.41                 |
| Hydrogen ....  | 6.91               | 6.65               | 6.81                 | 6.49               | 7.40              | 7.83                  |
| Oxygen, &c.... | 24.41              | 24.70              | 24.92                | 28.35              | 23.33             | 26.28                 |
| Nitrogen ..... | 18.15              | 18.19              | 17.58                | 14.01              | 14.78             | 14.48                 |
|                | 100.00             | 100.00             | 100.00               | 100.00             | 100.00            | 100.00                |

### PROTEINE.

Although, as has been remarked, there are certain distinctive peculiarities apparently belonging to each of the preceding substances, sufficient to establish them as separate proximate principles, yet the general resemblances which pervade them, long ago induced chemists to regard them as of common origin, and as deriving their peculiarities from small quantities of superadded substances, especially sulphur, phosphorus, and certain salts, rather than from any original and essential difference of quantitative ultimate composition. These views have been amply sanctioned by the discovery of the identity of the above compounds as derived from animals and vegetables, and more especially by the researches of Mulder, establishing the existence in all of them of a common base, which appears to derive its origin from the vital powers of plants, and to be transmitted from them to animals, as an essential part of their food; he has accordingly termed it *Proteine* (from *πρωτεύω*, to hold a chief place).

Proteine is obtained from albumine, fibrine, or caseine, or from horn, by digesting them successively in water, alcohol, and ether, so as to extract all soluble matters; the residue is then digested in dilute hydrochloric acid, by which the earthy salts are removed, and lastly, it is dissolved in a moderately strong solution of potassa or soda, which abstracts sulphur and phosphorus; this solution is then heated to 120°, and cold acetic acid is added in very slight excess, which throws down the proteine in the form of a gelatinous precipitate, which is to be thoroughly washed with water upon a filter.

Thus obtained, proteine is a translucent, gelatinous, inodorous and insipid substance, insoluble in cold and warm water, and in alcohol, ether, and volatile oils; when dry, it is brownish, hard, and brittle, and yields a yellow powder; it is very hygrometric, but becomes perfectly anhydrous when dried at 212°. When it is in this state digested in water, it reassumes its original gelatinous appearance.

When gradually heated to redness in close vessels, proteine affords the usual results of the decomposition of azotized organic substances, and leaves a bulky carbonaceous residue. The products of its ultimate

analysis, are, according to Mulder and Scherer (*Ann. der Pharm.*, xxviii. 73, and xL. 44) and Dumas and Cahours (*Chim. App. aux Arts*, vii. 439), as follows:

|               | From vegetable<br>Fibrine. | From animal<br>Fibrine. |            | From animal<br>Albumine. |            | From the<br>crystalline<br>Lens. | From<br>Horn. | Mean<br>result.       |  |
|---------------|----------------------------|-------------------------|------------|--------------------------|------------|----------------------------------|---------------|-----------------------|--|
|               | Mulder.                    | Mulder.                 | Scherer.   | Mulder.                  | Scherer.   | Scherer.                         | Scherer.      | Dumas and<br>Cahours. |  |
| Carbon ....   | 54.99 ....                 | 54.44 ....              | 54.85 .... | 55.32 ....               | 55.16 .... | 55.30 ....                       | 55.41 ....    | 54.94                 |  |
| Hydrogen .... | 6.87 ....                  | 6.95 ....               | 6.96 ....  | 6.96 ....                | 7.03 ....  | 6.94 ....                        | 7.24 ....     | 7.11                  |  |
| Oxygen ....   | 22.46 ....                 | 22.56 ....              | 22.34 .... | 21.68 ....               | 21.82 .... | 21.54 ....                       | 21.76 ....    | 22.02                 |  |
| Nitrogen .... | 15.66 ....                 | 16.05 ....              | 15.85 .... | 16.04 ....               | 15.99 .... | 16.22 ....                       | 15.59 ....    | 15.93                 |  |
|               | 100.00                     | 100.00                  | 100.00     | 100.00                   | 100.00     | 100.00                           | 100.00        | 100.00                |  |

From these analyses Mulder has deduced the formula  $C_{40}H_{30}O_{12}N_5$ , and Scherer  $C_{48}H_{36}O_{14}N_6$ . The agreement of these formulæ with the experiments is very close, as shown by the following table:

|               | Mulder. |      |     |      |        | Scherer.      |    |      |                 |
|---------------|---------|------|-----|------|--------|---------------|----|------|-----------------|
| Carbon .....  | 40      | .... | 240 | .... | 55.05  | Carbon .....  | 48 | .... | 288 .... 55.38  |
| Hydrogen....  | 30      | .... | 30  | .... | 6.88   | Hydrogen....  | 36 | .... | 36 .... 6.92    |
| Oxygen ....   | 12      | .... | 96  | .... | 22.02  | Oxygen ....   | 14 | .... | 112 .... 21.54  |
| Nitrogen .... | 5       | .... | 70  | .... | 16.05  | Nitrogen .... | 6  | .... | 84 .... 16.16   |
| Proteine .... | 1       |      | 436 |      | 100.00 | Proteine .... | 1  |      | 520 .... 100.00 |

In the one case the equivalent of proteine is 436, in the other 520; in the absence of any unequivocal experimental proofs, either of these may be adopted; the latter appears in some respects to be preferable, and closely approximates to the formula of Dumas and Cahours, which is  $C_{48}H_{36}O_{14}N_6 + H_2O$ ; but Mulder's formula is not inconsistent with the analyses of certain proteine compounds afterwards to be noticed.

When fibrine or coagulated albumine are heated in water under such pressure as to command a temperature of about  $390^{\circ}$  (L. GMELIN), or, according to Vogel and Wöhler, of  $300^{\circ}$ , (*Ann. der Pharm.*, xLi. 238,) they are almost entirely dissolved, and converted according to Mulder into *oxides of proteine*; and when those substances, or pure proteine, are boiled for a long time in pure water, some ammonia is evolved, and a soluble and insoluble product formed; the latter is extremely friable. By continuously boiling fibrine and albumine for 40 hours in water, they afforded

|                        | Fibrine. | Albumine. |
|------------------------|----------|-----------|
| Insoluble matter ..... | 79.33    | 63.08     |
| Soluble matter .....   | 20.67    | 36.92     |
|                        | 100.00   | 100.00    |

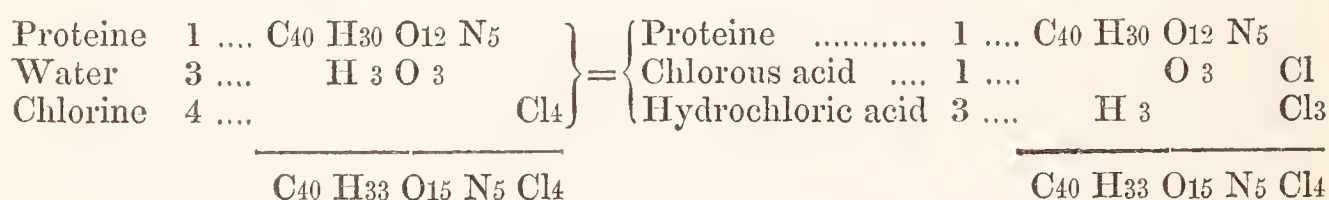
On evaporating the aqueous solution of the soluble matter, the residue is partly soluble in alcohol, and part remains undissolved; the portion insoluble in alcohol consists of proteine +  $O_3$ ; the soluble portion includes several products. The relative proportions of the part insoluble in alcohol to that which is soluble, are as follow:

|                            | Fibrine. | Albumine. |
|----------------------------|----------|-----------|
| Insoluble in alcohol ..... | 59.3     | 66.0      |
| Soluble in alcohol .....   | 40.7     | 34.0      |
|                            | 100.0    | 100.0     |
|                            |          | 4 M       |



When fibrine is boiled in water, the insoluble residue varies in composition with the time of boiling, and is either a mixture of unaltered fibrine and an *oxide of proteine*, consisting of 1 atom of proteine + 2 atoms of oxygen (*Binoxypoteine*), or only the latter. When, on the other hand, albumine is similarly treated, the residue is unaltered albumine; but in both cases the portion which is dissolved consists of 1 atom of proteine + 3 atoms of oxygen (*Trioxypoteine*). MULDER.

When chlorine is passed through water containing proteine or its compounds, (such as liquid albumine or caseine, or an ammoniacal solution of fibrine,) a white precipitate falls, composed of proteine and chlorous acid, the proteine undergoing, according to Mulder, no decomposition, while chlorous and hydrochloric acid are formed by the decomposition of water, under its influence: the hydrochloric acid dissolves the saline matters contained in the proteine compounds. This action is such, that 1 atom of proteine, 3 of water, and 4 of chlorine, produce 1 atom of chlorite of proteine and 3 of hydrochloric acid, as in the following equation:



This combination has been termed *Proteochlorous acid*. When thoroughly washed, and dried at  $212^\circ$ , it forms a yellow powder, greasy to the touch, almost insoluble in water, and insoluble in alcohol and ether: sulphuric acid dissolves it, and the solution lets fall a white precipitate when diluted. Heated upon platinum foil, the proteochlorous acid burns without residue, exhaling an odour like that of saffron.

When proteochlorous acid is dissolved in ammonia, nitrogen is evolved, and on evaporating the solution to dryness, dissolving the residue in hot water, and then adding alcohol, a yellow powder falls, which is trioxypoteine, and sal ammoniac remains in solution: so that the chlorine of the chlorous acid appears to combine with the ammonia, forming sal ammoniac and evolving nitrogen, while its oxygen unites to the proteine.

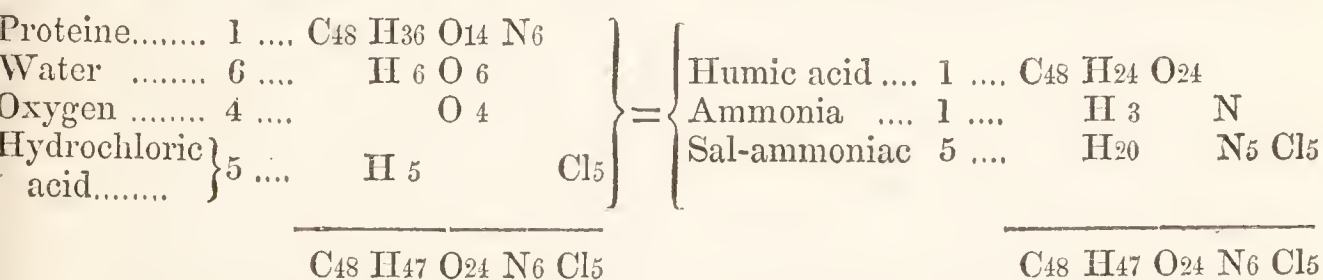
Proteochlorous acid is soluble in baryta water; and if carbonic acid be passed through the solution, and then heated and filtered, a liquor is obtained from which alcohol throws down a precipitate of *proteochlorite of baryta*, while chloride of barium remains in solution. When the solution of the barytic salt is added to a solution of nitrate of zinc, copper, iron, or lead, the precipitates which fall, are the *proteochlorites* of those metals.

*Action of acids on Proteine.* Hydrochloric acid appears to combine with proteine in several proportions. When that acid is dropped into an acetic solution of proteine, (albumine, or caseine,) a gelatinous substance separates, which, when washed with alcohol and carefully dried, is a compound of 2 atoms of proteine with 1 of hydrochloric acid. When proteine is digested in concentrated hydrochloric acid, it becomes gelatinous, and, as has been above stated, under the heads *Albumine*, *Caseine*, *Fibrine*, &c., it dissolves in the acid, forming a peculiar blue liquor, which, on the addition of water, yields a white precipitate, soluble in pure water. When moist proteine is digested in dilute hydrochloric

acid, the same compound appears to be formed: it consists, according to Mulder, of 1 atom of proteine combined with 1 of hydrochloric acid.

According to Mulder, the peculiar solution obtained by the action of hydrochloric acid on proteine and its compounds, and which becomes blue or purple by exposure to air, contains, in that state, sal ammoniac, ammonia, and humic acid. When proteine is digested for four days in hydrochloric acid, and the whole then evaporated at a temperature between  $140^{\circ}$  and  $160^{\circ}$ , a brown coagulum separates, which is perfectly soluble in pure water, and consists of 2 atoms of proteine + 3 of hydrochloric acid. The liquor poured off the coagulum leaves, on evaporation, a dark substance, which, when carefully dried at  $212^{\circ}$ , becomes, on cooling, hard, and brittle, but is very attractive of moisture; it is almost entirely soluble in water, with the exception of a small portion of brown matter, which separates, and which is *humic acid*; the solution contains sal ammoniac and humate of ammonia. Mulder supposes that the blue liquor resulting from the action of hydrochloric acid upon proteine and its modifications, contains a double salt, consisting of sal ammoniac and humate of ammonia.

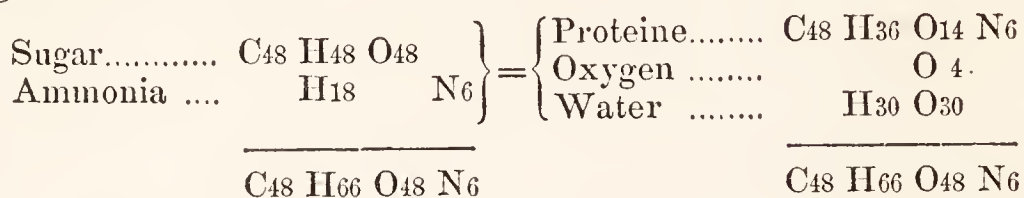
This formation of humic acid during the action of hydrochloric acid upon proteine, has been adduced in illustration of the original formation of proteine in vegetables. Dr. Gregory (*Outlines*, p. 539) illustrates this subject as follows, using Liebig's equivalents for proteine and humic acid.



"This reaction enables us to see how proteine might be formed from the elements of sugar and ammonia, water and oxygen being eliminated. For, abstracting the hydrochloric acid, and bearing in mind that humic acid, C<sub>48</sub> H<sub>24</sub> O<sub>24</sub>, is merely sugar minus water, anhydrous grape sugar being C<sub>12</sub> H<sub>12</sub> O<sub>12</sub>, and 4 equivalents of it being equal to C<sub>48</sub> H<sub>48</sub> O<sub>48</sub>; let us then suppose 4 equivalents of grape sugar to lose half the water they contain, leaving this variety of humic acid, and to take up 6 equivalents of ammonia. Let us further pursue the process which is opposite to that above explained, and subtract 4 equivalents of oxygen and 6 of water, and proteine will remain. The reader will observe that we can actually, with the aid of hydrochloric acid, cause proteine to take up oxygen and water, and produce ammonia and humic acid, and that this humic acid only differs from sugar by the elements of water. So that we may expect hereafter to reverse the process, and to cause sugar or humic acid, taking up ammonia and giving off water and oxygen, to give rise to proteine. At all events, it is evident that proteine might thus be derived from sugar and ammonia, which meet in plants; and although in general we are unable artificially to produce the more complex substances, and can only decompose or resolve them into less complex forms, yet there are even now some cases in which more complex molecules may be artificially formed by the coalescence of more simple ones; and it is probably in these very circumstances that the vital force interferes and modi-



fies the results. We may represent as follows the conceivable change (the converse of that actually observed,) by which proteine may originate from sugar and ammonia."



When nitric acid is added to a dilute alkaline solution of proteine, (or albumine,) a white precipitate falls, soluble in pure water, which is a compound of proteine and nitric acid. The further properties of this and similar compounds, and the formation of *xanthoproteic acid*, have been already adverted to (p. 1229).

When pulverized proteine is added to concentrated sulphuric acid, it gradually forms a bulky jelly, from which water separates excess of acid and leaves a contracted mass, which becomes hard on drying, and is insoluble in water, alcohol, and ether. When it has been washed with water till the washings no longer precipitate barytic solutions, it has no acid reaction; it appears to be a true *sulphate of proteine*, having the formula  $\text{C}_{40} \text{H}_{30} \text{O}_{12} \text{N}_5 + \text{SO}_3$ ; but, as it combines with bases, and constitutes definite salts, Mulder has termed it *proteosulphuric acid*. Its neutral solution in dilute alkalis does not affect the salts of lime or baryta, but it occasions precipitates in the solutions of sulphate of iron and of copper, and nitrate of silver. The silver salt is  $\text{AgO} + (\text{C}_{40} \text{H}_{30} \text{O}_{12} \text{N}_5 + \text{SO}_3)$ . The copper salt is a basic hydrated double salt, to which Mulder assigns the formula  $5\text{CuO} + \text{C}_{40} \text{H}_{30} \text{O}_{12} \text{N}_5 + 2\text{SO}_3 + 3\text{HO}$ .

*Action of Alkalis on Proteine.* When the dilute alkaline solutions of proteine are mixed with alcohol, a compound of proteine with the alkaline base is thrown down. The compounds of proteine with the earths and heavy metallic oxides are insoluble, and are thrown down on adding a solution of the metallic salt to an acetic solution of proteine. These compounds are stated by Mulder to consist of 1 atom of the respective bases, combined with 10 atoms of proteine. But if acetate of lead be added to a solution of proteine in great excess of acetic acid, the compound which falls contains 20 atoms of proteine to 1 of oxide of lead. The composition of these precipitates, however, seems liable to too many variations to enable us to assign to them satisfactory formulæ.

When proteine or its compounds are boiled in a moderately strong solution of potassa till ammonia is no longer disengaged, and the liquor after it has cooled is saturated by sulphuric acid, sulphate of potassa is formed, the greater part of which may be separated by crystallization; if the remaining solution is then poured off and evaporated to dryness, and the residue boiled in repeated portions of alcohol, it leaves sulphate of potassa, and dissolves the organic products: as this alcoholic solution cools, it lets fall a brown oleaginons matter (*erythroprotide*), and afterwards, on spontaneous evaporation, it deposits *leucine*, and retains *protide*, mixed with formiate of potassa, in solution.

*Erythroprotide*,  $\text{C}_{13} \text{H}_8 \text{O}_5 \text{N}$ , when purified by repeated solution in boiling alcohol, is a soft red substance of a slightly bitter taste, very soluble in water, but not deliquescent, and scarcely at all soluble in cold alcohol: its aqueous solution is precipitated by acetate of lead, corrosive

sublimate, and nitrate of silver, and also by tincture of galls. It consists, according to Mulder, of

|                      |    |     |     |     | Mulder. |
|----------------------|----|-----|-----|-----|---------|
| Carbon .....         | 13 | ... | 78  | ... | 55.71   |
| Hydrogen.....        | 8  | ... | 8   | ... | 5.71    |
| Oxygen.....          | 5  | ... | 40  | ... | 28.58   |
| Nitrogen .....       | 1  | ... | 14  | ... | 10.00   |
| <hr/>                |    |     |     |     |         |
| Erythroprotide ..... | 1  |     | 140 |     | 100.00  |

*Protide*, C<sub>13</sub> H<sub>9</sub> O<sub>4</sub> N, remains, as above stated, in solution with formiate of potassa; to separate it the liquor is diluted with water, and a solution of acetate of lead added till it no longer occasions a precipitate. This precipitate consists of protide in combination with oxide of lead; after having been well washed, it may be diffused in water, and decomposed by a stream of sulphuretted hydrogen; the protide remains in solution, which, filtered and evaporated, leaves it in the form of a yellowish amorphous and friable substance, very soluble in water; it also dissolves in cold alcohol; it has a bitter taste, and its aqueous solution is precipitated by basic acetate of lead, but not by corrosive sublimate, nitrate of silver, or tincture of galls. Mulder found protide to consist of

|                |    |     |     |     | Mulder. |
|----------------|----|-----|-----|-----|---------|
| Carbon.....    | 13 | ... | 78  | ... | 58.65   |
| Hydrogen ..... | 9  | ... | 9   | ... | 6.76    |
| Oxygen .....   | 4  | ... | 32  | ... | 24.06   |
| Nitrogen ..... | 1  | ... | 14  | ... | 10.53   |
| <hr/>          |    |     |     |     |         |
| Protide.....   | 1  |     | 133 |     | 100.00  |

*Leucine*, C<sub>12</sub> H<sub>12</sub> O<sub>4</sub> N. The deposition of leucine from the alcoholic solution of protide has been above mentioned; but this substance is not only the result of the action of the caustic alkalis upon proteine and its compounds; it is also formed, as Braconnot first showed, by the action of sulphuric acid upon gelatine (*Ann. Ch. et Ph.*, xiii. 113;) and Mulder has detected it among the products of the putrefaction of caseine.

Leucine has a pearly lustre, and much resembles cholesterine in appearance; it is friable, tasteless, inodorous, and greasy to the touch, and sublimes before fusion, and without decomposition, at about 340°. It is soluble in about 28 parts of water at 65°, and in 658 parts of alcohol of the specific gravity 0.828, and at the same temperature; a saturated solution in boiling alcohol becomes turbid on cooling; it is insoluble in ether; it is anhydrous, and neither acid nor alkaline. Leucine is soluble without decomposition in concentrated sulphuric and hydrochloric acids. Chlorine decomposes it, forming hydrochloric acid and other products, among which is a brown resinoid substance, and a red volatile liquid. It absorbs hydrochloric acid gas, forming with it a monoatomic combination. Its composition, as determined by Mulder, is as follows:—

|                |    |     |     |     | Mulder. |
|----------------|----|-----|-----|-----|---------|
| Carbon.....    | 12 | ... | 72  | ... | 55.39   |
| Hydrogen ..... | 12 | ... | 12  | ... | 9.23    |
| Oxygen .....   | 4  | ... | 32  | ... | 24.62   |
| Nitrogen ..... | 1  | ... | 14  | ... | 10.76   |
| <hr/>          |    |     |     |     |         |
| Leucine .....  | 1  |     | 130 |     | 100.00  |



When a solution of leucine in warm nitric acid is carefully evaporated, it deposits small white crystals, which, when purified by solution in water and recrystallization, constitute the *Nitroleucic acid*  $=C_{12}H_{13}O_{10}N_2$ ; it was discovered by Braconnot, and analyzed by Mulder; it combines with bases, and its salts deflagrate when heated: its proximate constituents appear to be

|                        |   |     |     |     |        |
|------------------------|---|-----|-----|-----|--------|
| Leucine .....          | 1 | ... | 130 | ... | 67·37  |
| Nitric acid .....      | 1 | ... | 54  | ... | 27·98  |
| Water .....            | 1 | ... | 9   | ... | 4·65   |
| <hr/>                  |   |     |     |     |        |
| Nitroleucic acid ..... | 1 |     | 193 |     | 100·00 |

## § VII. GELATINE. CHONDRINE.

THESE substances, like those embraced in the last Section, are characterized as containing a large relative proportion of nitrogen; but, unlike the proteiniferous compounds, their production is limited to the animal creation; they are, however, not found in the blood, but are exclusively products of secretion: they are nutritive; and are in all probability products of the change of proteine on the one hand, and on the other, reconvertible into proteine, by vital processes. When the skin, and cellular and other membranes of animals are boiled in water, the resulting liquor *gelatinizes* on cooling, and a similar jelly may be obtained from bones, cartilages, tendons, and ligaments. The term *gelatine* was long indiscriminately applied to all the substances thus obtained, until Müller pointed out the peculiarities of the product derived from *cartilage*, and appropriated to it the term *Chondrine*. (*Poggend. Ann.*, xxxviii. 305.) It is generally assumed, though not perhaps on very sufficient grounds, that the gelatigenous textures do not contain ready-formed *gelatine*; that that substance does not, in fact, pre-exist in the animal kingdom, but that it is generated by the action of hot water upon the membranous tissues.

To obtain *gelatine*, the substances affording it, such as the clippings of hides, hoofs, horns, calves' feet, cows' heels, sheep's trotters, pigs' pettoes, certain membranes, &c., are cleansed in cold water, and then subjected to the action of boiling water; the solution so obtained is freed from fat, and from any deposit, by skimming and straining, and allowed to gelatinize on cooling: the jelly so formed is known under the name of *size*; when cut into slices and dried, it is called *glue*.

The purest form of commercial *gelatine* is *isinglass*; it is largely consumed as an article of food, and is chiefly prepared in Russia from the air-bladders and sounds of certain species of *Acipenser*, or sturgeon. These membranous tissues are cleansed, dried, and scraped, forming *leaf isinglass*; or they are twisted up into various forms, as that of a heart or horseshoe, termed long and short *staple*; or folded into packages, constituting *book isinglass*. An inferior article imported from America, called *Ribbon isinglass*, is prepared from the intestines of the cod. *Isinglass* was formerly picked into shreds, but is now usually cut into delicate filaments by machinery. It should be colorless, inodorous, and perfectly soluble in hot water: when incinerated, it leaves a mere trace of phosphate

of soda and phosphate of lime. (For a description of the commercial varieties and values of isinglass, see "PEREIRA on Food and Diet.")

*Size* is usually sold in the form of a stiff tremulous jelly; it is obtained from the above-mentioned sources, and also from the waste of vellum, parchment, and some kinds of white leather, and from the skins of horses, cats, dogs, and rabbits, and sometimes from fish. It is largely employed in the manufacture of paper, and by white-washers, painters in distemper, paper-stainers and gilders. Size has usually a putrid odor and taste, and a brown color, but it may be rendered inodorous, insipid, and colorless, by the careful application of sulphurous acid, and when thus purified and dried in thin layers, forms a good and common substitute for isinglass. It is sometimes tinged of different colors, and sold under the name of *patent gelatine*, *greneline*, &c.

*Glue* is an important article of manufacture, and differs in price and quality according to its source. It is extracted from bones, muscles, tendons, ligaments, membranes, and skins, the latter yielding the best glue, especially when from old animals. The parings of hides and pelts from tanners and furriers, the hoofs and ears of horses, oxen, calves, sheep, &c., are the substances from which it is extracted in Britain. They are first digested in lime water, then washed, laid in a heap to drain, and boiled in soft water; the impurities are carefully skimmed off, and the liquor is then strained, clarified with a little alum, and allowed to settle; it is then poured off from the sediment, and boiled down to a proper consistence, so as to concrete on cooling: it is then cut by a wire into slices, which are dried upon netting. Good glue is hard, brittle, of an uniform brown translucency, and when immersed for some time in cold water, becomes gelatinous, but requires to be heated, so as to dissolve and fit it for use; this should be done over a gentle fire, or in a water bath, and it may then be applied to the wood by a stiff brush: it will not harden in a freezing temperature; the adhesion depends upon the absorption and evaporation of the superfluous water. According to Bostock, glue, in its ordinary state of dryness, retains about 10 *per cent.* of water. (*Nicholson's Journ.*, xxiv. 7.)

*Gelatine of Bones* is obtained by heating ground or rasped bones with water, under pressure, to a temperature of  $250^{\circ}$  to  $270^{\circ}$ ; the liquor gelatinizes on cooling, and the jelly may be purified as in the previous cases. But the gelatine thus obtained always retains a disagreeable flavor in consequence of the high temperature employed. Another mode of obtaining bone jelly consists in digesting the bones, previously boiled to remove the fat, in dilute hydrochloric acid, so as to abstract the phosphate of lime; the animal part of the bone is thus left, having the appearance of a tough flexible cartilage, and when thoroughly washed in water, is steeped in lime water, or in a weak solution of carbonate of soda, and again washed and dried. This dried bone-gelatine may then be made into glue or size by boiling, gelatinizing, and drying, as with the other forms of gelatine. The acid liquor, saturated with carbonate of lime, furnishes an admirable manure. (In reference to the economy and details of these different processes, see DUMAS, *Chim. App. aux Arts*, vii. 412.) Gelatine obtained from hartshorn shavings (*hartshorn jelly*) is tasteless, and has the advantage of freedom from fat.

*Pure gelatine* is colorless, transparent, inodorous, and insipid; it has



a peculiar toughness, varying, however, in cohesion, with its source. It is heavier than water. When heated it softens, then shrinks and exhales a peculiar odor, burning difficultly, and exhaling the odor of burned horn or feathers. Subjected to destructive distillation, it yields abundance of carbonate of ammonia, together with the other usual products of azotised organic matters, and leaves a bulky coal difficult of incineration.

In cold water gelatine gradually softens and swells, but scarcely dissolves till gently heated, and on again cooling the solution forms a more or less firm jelly. The best glue absorbs by immersion in cold water three or four times its weight, without dissolving; where less water is absorbed, or where the glue loses its viscidness in cold water, it is unfit for use. According to Bostock 1 part of isinglass dissolved in 100 of water, gelatinises on cooling; but in 150 of water it remains liquid. (*Nicholson's Journ.*, xi. and xiv.) But this effect, as is well known, varies much with temperature, so that jellies are much easier prepared in winter than in summer. The stiffness of the jelly is also greatly dependent upon the source whence it was originally obtained; the skins and tissues of old animals yielding a stronger and firmer jelly than that derived from young ones.

When a solution of gelatine is repeatedly warmed and cooled, more especially if it be boiled, it gradually loses its tendency to gelatinise, and becomes more and more soluble. According to Goudoever and Mulder, (*Poggend.*, xxxvii. and xl., and *Ann. der Pharm.*, xl. 48,) a peculiar atomic compound of 1 atom of water and 4 of gelatine may be formed by boiling a solution of isinglass in water for 55 hours; it does not jelly on cooling, and when evaporated leaves a white pulverulent residue. When a solution of gelatine is hermetically sealed up in a tube and left for some weeks in boiling water, it loses its power of gelatinising, and leaves on evaporation a viscid deliquescent substance, very soluble in water and partially soluble in alcohol. (L. GMELIN.)

In close vessels jelly may be kept in cool weather for some days without change; but in open vessels it soon becomes mouldy, (especially in the vicinity of blossoming plants. *Ann. der Pharm.*, xli. 236.) It then putrefies and exhales a disagreeable ammoniacal odor. A little acetic acid considerably retards these changes without materially affecting its gelatinisation.

{ Gelatine is not soluble in absolute alcohol, and when alcohol is added to a warm and strong aqueous solution, the gelatine separates in the form of a white viscid substance. It is insoluble in ether, and in fixed and volatile oils. When common gelatine, glue for instance, is digested in alcohol, it yields a little fat and extractive matter to that solvent. When jelly is immersed in alcohol it contracts very considerably in consequence of the abstraction of water; it was thus that Gonner applied it for the reduction in size of the impression of lithographic prints; and on the other hand, when the original impression was taken upon dehydrated or contracted gelatine, it could be so dilated by immersion in water, as to give a greatly enlarged impression of a small print.

Many and somewhat discordant ultimate analyses of gelatine have been made by Scherer, Mulder, Goudoever, and others, and several formulæ have been proposed for it: the following, which appears to be

that adopted by Löwig, (*Chem. der Organ. verbind.*) seems the most consistent with the experimental results, and with such atomic combinations of gelatine as have been at all accurately examined.

|                |    |     |        |        | Mulder. | Scherer. | Scherer. | Goudoever. |
|----------------|----|-----|--------|--------|---------|----------|----------|------------|
| Carbon .....   | 13 | 78  | 50.00  | 50.04  | 50.4    | 50.78    | 50.00    |            |
| Hydrogen.....  | 10 | 10  | 6.41   | 6.47   | 6.9     | 7.15     | 6.72     |            |
| Oxygen .....   | 5  | 40  | 25.64  | 25.13  | 23.8    | 23.75    |          |            |
| Nitrogen ..... | 2  | 28  | 17.95  | 18.36  | 18.9    | 18.32    |          |            |
| <hr/>          |    |     |        |        |         |          |          |            |
| Gelatine ..... | 1  | 156 | 100.00 | 100.00 | 100.0   | 100.00   |          |            |

When chlorine is passed through a warm and moderately strong solution of isinglass, each bubble becomes enveloped in a white film, which it deposits as it bursts upon the surface, forming a white, elastic, and coherent scum, having a strong odor of chlorous acid, which it evolves when dried at  $212^{\circ}$ , leaving a brown residue. Acted upon by ammonia, nitrogen is evolved, sal ammoniac produced, and unaltered gelatine separated. This matter is composed, according to Mulder, of 1 atom of gelatine +  $\text{Cl}_2 \text{O}_3$ . There is a gelatinous opalescent substance formed at the same time, which falls as a precipitate, and which consists of 3 atoms of gelatine +  $2\text{Cl}_2 \text{O}_3$ . Mulder has described two other chlorous compounds, being respectively 4 gelatine +  $\text{Cl}_2 \text{O}_3$ , and 5 gelatine +  $2\text{Cl}_2 \text{O}_3$ . (*Ann. der Pharm.*, xxxi. 332.) Neither bromine nor iodine produce any analogous combinations.

Gelatine is soluble in all the dilute acids, differing essentially in this respect from albumine: of these, the acetic solution only gelatinises on evaporation.

When the dilute nitric solution of gelatine is evaporated, nitrous gas is evolved, and the residue deflagrates just before dryness: with strong nitric acid, oxalic acid is formed. The action of sulphuric acid on gelatine is attended by the formation of leucine, and of a peculiar saccharoid product, which will presently be noticed.

The dilute caustic alkalis, and ammonia, do not prevent the gelatinisation of gelatine, but they often throw down a portion of phosphate of lime. When gelatine is dissolved in a cold dilute solution of caustic potassa, and exactly neutralised by acetic acid, the evaporated liquor does not gelatinise in cooling; it leaves a residue of altered gelatine combined with acetate of potassa, which is soluble in alcohol, and from this solution sulphuric acid throws down a mixture of sulphate of potassa with modified gelatine.

When gelatine is boiled with caustic potassa, ammonia is evolved, and leucine (p. 1241) and gelatine-sugar are formed. Gelatine is not altered by boiling with hydrated lime.

Neutral persulphate of iron is not affected by a solution of gelatine, unless boiled, when a precipitate falls, composed, according to Mulder, of 3 atoms of gelatine, 6 of oxide of iron, and 1 of sulphuric acid. A solution of gelatine is not precipitated either by the neutral acetate, or by subacetate of lead (DUMAS), but, according to Gmelin, subacetate of lead occasions a copious precipitate. With protochloride of tin it gives a brown flocculent precipitate, but none with the perchloride. When a solution of gelatine is gradually added to one of corrosive sublimate, a cloud is formed which at first disappears, but afterwards a coherent elastic sub-



stance is thrown down. The nitrates of mercury produce the same effect. Gelatine is not precipitated by solution of silver or of gold, but sulphate of platinum throws it down in brown viscid flakes, which blacken and become brittle when dried on a filter. E. Davy recommends this as a very delicate test of gelatine, detecting it in solutions too weak to be affected by tannine, and not interfered with by the presence of albumine. (*Phil. Trans.*, 1820, p. 119.) Neither sulphate of alumina nor alum occasion any precipitate in solution of gelatine, but a mixture of chloride of sodium and alum, or a solution of chloride of aluminum, form a white precipitate: this compound exists in *tawed leather*.

Tannine is a most delicate test of the presence of gelatine; when it is added to a solution of 1 part of gelatine in 5000 of water, a cloud is evident, and on dropping tincture or fresh infusion of galls into a strong solution of gelatine, a dense white curdy precipitate of tannogelatine falls, which becomes grey when dried, and is insoluble in water, and not putrescible. Mulder has described two definite combinations of tannine with gelatine; 1, containing 1 atom of gelatine and 1 of tannine, is thrown down when great excess of tannine is used; and 2, containing 3 atoms of gelatine and 2 of tannine, formed when the tannine is not added in excess. According to Davy, when gelatine is precipitated with infusion of oak bark, 100 parts of the precipitate contain 54 of gelatine and 46 of tannine. Schiebel found that when a solution of 100 parts of gelatine is precipitated by a great excess of an infusion of 1 part of oak bark in 9 of water, it combines with 118 parts of tannine; but when a weak solution of extract of oak bark is added to a solution of gelatine so as not to precipitate the whole of the latter, the precipitate which slowly falls contains 100 of gelatine and 60 of tannine. (*Ann. der Pharm.*, xxxi. 124.) It will be recollected that albumine may also be precipitated by tannine, and that therefore in using it as a test of gelatine, the absence of albumine should be previously ascertained.

*Sugar of gelatine.* This curious compound was discovered by Braconnot. (*Ann. Ch. et Ph.*, xiii. 113.) 1 part of pulverised glue was mixed with 2 of concentrated sulphuric acid; after having been left together for 24 hours, during which time no discoloration had ensued, 8 parts of water were added and the mixture boiled for five hours, occasionally renewing the water. The liquor was then further diluted and saturated by chalk, filtered, and evaporated, when it yielded a syrup which, set aside for a month, produced small sweet crystals; these were washed with weak alcohol to separate the adhering syrup, and further purified by a second crystallization. This substance requires 414 parts of water, and 930 of alcohol (sp. gr. 0.828) at 65°, for solution. The alcoholic solution left to spontaneous evaporation, yields large prismatic crystals; but if the alcohol be diluted, the crystals are rhomboids. The saturated solution in hot alcohol becomes turbid as it cools. When heated to 230° gelatine-sugar loses no water, but when mixed with oxide of lead 2 atoms of water are evolved. (MULDER.) According to Mulder the formula of crystallized gelatine-sugar is  $C_8 H_7 O_5 N_2 + 2HO$ . According to Boussingault it is  $C_{16} H_{15} O_{11} N_4 + 3HO$ . The following is Mulder's analysis. (LÖWIG, *Ch. Org. verb.*, i. 627.)

|                                  |   |     |     |     |        | Mulder. |        |
|----------------------------------|---|-----|-----|-----|--------|---------|--------|
| Carbon .....                     | 8 | ... | 48  | ... | 34·04  | ...     | 34·06  |
| Hydrogen .....                   | 9 | ... | 9   | ... | 6·38   | ...     | 6·49   |
| Oxygen .....                     | 7 | ... | 56  | ... | 39·72  | ...     | 39·61  |
| Nitrogen .....                   | 2 | ... | 28  | ... | 19·86  | ...     | 19·84  |
| <hr/>                            |   |     |     |     |        |         |        |
| Crystallized gelatine-sugar .... | 1 |     | 141 |     | 100·00 |         | 100·00 |

When gelatine-sugar is heated to about  $350^{\circ}$ , it begins to fuse and be decomposed, evolving the products of azotised organic matter, and leaving a bulky coal which burns away without residue.

Subjected to the action of chlorine at common temperatures, water, hydrochloric acid, and a brown substance resembling that obtained by the action of chlorine upon leucine, are formed; and a sour liquid is at the same time produced, which yields prismatic crystals not as yet examined. Bromine and iodine appear to act in the same way as chlorine. (MULDER.)

The aqueous solution of gelatine-sugar produces no precipitate in sulphate of copper, acetate of lead, nitrate of mercury, or nitrate of silver. A soluble and insoluble compound with oxide of lead may be formed by boiling them together; the former yields delicate prismatic crystals, having the formula  $4\text{PbO} + \text{C}_{16}\text{H}_{15}\text{O}_{11}\text{N}_4$ . Corresponding compounds were obtained with oxide of copper and oxide of silver. (BOUSSINGAULT.)

*Nitrosaccharic acid* was obtained by Braconnot by dissolving gelatine-sugar in warm nitric acid; on cooling, crystals are deposited, which are generally rhombic, having a sour and sweet taste, soluble in water, but insoluble in alcohol. It frequently happens that the nitric solution does not crystallize till agitated, and then suddenly concretes. Mulder represents this acid as a compound of 1 atom of gelatine-sugar, 2 of nitric acid, and 4 of water; its empyric formula being  $\text{C}_8\text{H}_{11}\text{O}_{19}\text{N}_4$ . Boussingault, doubling the equivalent of gelatine-sugar, considers the nitrosaccharic acid as including 1 atom of gelatine-sugar, 4 of nitric acid, and 2 of water, whence he derives the formula  $\text{C}_{16}\text{H}_{17}\text{O}_{33}\text{N}_8$ . Mulder represents the baryta salt by the formula  $2(\text{BaO}, \text{NO}_5) + (\text{BaO}, \text{C}_8\text{H}_6\text{O}_5\text{N}_2)$ , while the formula adopted by Boussingault for the potassa salt is  $4\text{KO}, + \text{C}_{16}\text{H}_{17}\text{O}_{33}\text{N}_8$ . The nitrosaccharate of copper and of silver have also been analysed by Boussingault.

**CHONDRINE.** When any of the permanent cartilages of the body, as those of the ribs, joints, and larynx, are boiled for several hours in water, they yield a liquor which jellies on cooling, but which contains a substance distinct from gelatine. To obtain it in its purest form, the cartilages of the ribs may be cut into small pieces and boiled in water for about 24 hours; the liquor is then evaporated and the gelatinous residue redissolved in hot water, filtered, and again evaporated; the product is finally digested in alcohol, or in ether, to remove all traces of fat, and pure chondrine remains. (MÜLLER.)

Chondrine, in its dry state, closely resembles gelatine; its solution in hot water gelatinizes when cold, and the greater number of reagents act upon it as upon gelatine. Its distinctive characters are, according to Müller, as follow: it is thrown down from its solutions by sulphate of alumina, and by alum, in white compact flakes, which easily cohere;



they are insoluble in hot and cold water, but soluble in excess of the precipitant, and a very small quantity of the aluminous salt is capable of effecting the precipitation of much chondrine. Acetic acid throws down chondrine, and the precipitate is not redissolved by excess of the acid; when, however, it is saturated by carbonate of potassa, the whole is redissolved. The aluminous precipitates are also redissolved on the addition of large quantities of solution of acetate of potassa, acetate of soda, and chloride of sodium. Persulphate of iron occasions a copious precipitate in solution of chondrine, which redissolves in excess of the precipitant, aided by heat. Acetate of lead forms a permanent precipitate in solution of chondrine. When a very minute quantity of hydrochloric acid is added to a solution of chondrine, a precipitate is formed, which is easily soluble in slight excess of the acid: ferrocyanide of potassium does not precipitate this acidulated liquor. The solution of chondrine is not affected by caustic alkalis; it is precipitated slightly by chloride of platinum, but not by nitrate of silver. Tartaric, citric, and oxalic acid form permanent precipitates in solution of chondrine.

Chondrine has been analysed by Mulder, Schröder, and Vogel, (*Journ. de Pharm.*, Août, 1841,) and by Scherer. (*Ann. der Pharm.*, XL. 50.) It has been represented as follows:—

|                 |    |     |     |     |        | Mulder. |       | Vogel. |       | Schröder. |       |
|-----------------|----|-----|-----|-----|--------|---------|-------|--------|-------|-----------|-------|
| Carbon .....    | 32 | ... | 192 | ... | 49·74  | ...     | 49·96 | ...    | 48·97 | ...       | 49·93 |
| Hydrogen .....  | 26 | ... | 26  | ... | 6·73   | ...     | 6·63  | ...    | 6·53  | ...       | 6·61  |
| Oxygen .....    | 14 | ... | 112 | ... | 29·02  | ...     | 28·59 | ...    | 29·63 |           |       |
| Nitrogen ....   | 4  | ... | 56  | ... | 14·51  | ...     | 14·44 | ...    | 14·55 |           |       |
| <hr/>           |    |     |     |     |        |         |       |        |       |           |       |
| Chondrine ..... | 1  |     | 386 |     | 100·00 |         | 99·62 |        | 99·68 |           |       |

The deficiency of 0.38, and 0.32, in the analyses of Mulder and Vogel, is the amount of sulphur; hence Vogel's formula for chondrine is  $5(\text{C}_{32} \text{H}_{26} \text{O}_{14} \text{N}_4) + \text{S}$ . Liebig represents chondrine as  $= \text{C}_{48} \text{H}_{40} \text{O}_{20} \text{N}_6$ , and containing, therefore, according to this formula, the elements of 1 atom of proteine and 4 of water + 2 oxygen. (*Organic Chem.*, Gregory's Ed., 126.)

|                  |   |  |
|------------------|---|--|
| 1 atom proteine  | = | $\text{C}_{48} \text{H}_{36} \text{O}_{14} \text{N}_6$ |
| 4 „ water        | = | $\text{H}_4 \text{O}_4$                                |
| 2 „ oxygen       | = | $\text{O}_2$   |
| <hr/>            |   |  |
| 1 atom Chondrine | = | $\text{C}_{48} \text{H}_{40} \text{O}_{20} \text{N}_6$ |

## § VIII. FATS AND FIXED OILS. FAT ACIDS. GLYCERINE.

THESE substances are common to vegetables and animals; they chiefly occur in the cellular structure of the seeds of the former, and contribute, in the opinion of some chemical physiologists, to the production of heat during germination, by undergoing oxidizement, or a species of slow combustion. In animals, they are principally deposited in the cellular membrane. They are of various degrees of consistence, varying from that of thin oil, as almond or spermaceti oil, to that of lard, or suet; the concrete oils of vegetables are frequently designated *vegetable butters*, as that of the coconut and nutmeg. These varieties often occur in the same plant and animal.

The vegetable oils are generally obtained by pressure, the seed being previously ground or bruised; and the expression of the oil is sometimes aided by increase of temperature. In animals the adipose cells are easily ruptured by heat, which liquefies and expands the fat, so that it runs out, or collects upon the water in which it is boiled. When, either in vegetable or animal products, the proportion of fat is very small, it is usually separated, (in quantitative analysis, for instance,) by the solvent power of alcohol, or of ether.

Little was known of the true nature of fats previous to the admirable researches of Chevreul, (*Sur les Corps Gras*, Paris, 1823,) who showed them to be compounds of peculiar acids, with a base termed *glycerine*, and that the common *soaps* are the same acids combined either with soda or potassa. The three principal acids which thus occur, are the *stearic*, the *margaric*, and the *oleic* acids; and the *stearate*, the *margarate*, and the *oleate* of glycerine, are generally termed *stearine*, (from *στεαρ*, *suet*,) *margarine*, (from *μαργαρον*, *a pearl*,) and *elaine*, (from *ελαιον*, *oil*.) It is upon the prevalence of one or other of these ingredients that the consistence of the fat depends; *stearine*, or *margarine* prevail in the solid fats, and *elaine* in the liquid oils.

Fats and oils are generally either colorless, or slightly yellow, but may be bleached by the protracted action of light. They are of themselves, for the most part, without smell or taste; but some of them have peculiar odors, dependent upon the presence of certain *volatile acids*; thus, butter contains *butyric acid*; goat's fat, *hircic acid*; whale oil, *phoenic acid*, &c. These, and the previously mentioned acids, together with others which are peculiar to certain oils and fats, will be separately described hereafter.

The specific gravity of fats is always below that of water; and it varies much with their temperature, for they are very expansive, and admit of being highly heated without decomposition.

According to Saussure, (*Ann. Ch. et Ph.*, xiii. 351,) the sp. gr. of common hog's lard, at 60°, is 0·938; in its fluid state, at 122°, it is 0·892; at 155°, it is 0·881, and at 200°, 0·863. The specific gravity of

|                  | At 53° |       | At 75° |       | At 122° |       | At 200° |
|------------------|--------|-------|--------|-------|---------|-------|---------|
| Nut oil is ..... | 0·928  | ..... | 0·919  | ..... | .....   | ..... | 0·871   |
| Almond oil.....  | 0·920  | ..... | .....  | ..... | .....   | ..... | 0·863   |
| Linseed oil..... | 0·939  | ..... | 0·930  | ..... | 0·921   | ..... | 0·881   |
| Castor oil ..... | 0·970  | ..... | 0·957  | ..... | .....   | ..... | 0·908   |
| Olive oil.....   | 0·919  | ..... | 0·911  | ..... | 0·893   | ..... | 0·862   |

The congealing and fusing points of the different oils and fats, and of their components, will be adverted to under their individual description. When they are subjected to higher temperatures, their colors are deepened, they exhale vapor, and at between 500° and 600° they begin to suffer decomposition, without which they cannot be distilled: the point at which these changes commence, and at which they appear to enter into a kind of ebullition, has been improperly termed their *boiling-points*; the glycerine which they contain is then decomposed; the fat acids are either resolved into new volatile products, or are themselves volatilized; variable quantities of carburetted hydrogen and of carbonic acid are evolved; and a small residue of carbon remains. During this distilla-



tion, the oleic acid of the fats is partially converted into sebacic acid, and their stearic acid into margaric acid; while the glycerine, by its decomposition, gives rise to an acrid irritating vapor, which Berzelius has named *Acroleine*; these effects of heat vary, however, with the nature of the oil.

*Acroleine* is not produced during the destructive distillation of the pure fat acids, so that its formation appears to result from the decomposition of glycerine. When the volatile products arising from the destructive distillation of olive oil or of hog's lard are passed through successive bottles half filled with water, the second and third bottles retain the greater portion of the acroleine, partly in the form of floating oil and partly dissolved in the water. When this floating oil is agitated with about twenty times its bulk of water, the greater part of it is dissolved, and when this solution is distilled in a water-bath, an oily matter passes over at about  $125^{\circ}$ , which is soluble in water, and which has the pungent odor of acroleine. It rapidly absorbs oxygen from the air, and becomes acid. When preserved out of contact of air, it changes into a white flocculent inodorous substance, insoluble in ether, oils, acids, and alkalis. The aqueous solution of acroleine gradually undergoes similar changes. (BERZELIUS. LIEBIG.)

When the vapor of fats or oils is made slowly to traverse a red-hot tube, it yields some of the above-mentioned products, together with a considerable quantity of liquid, vaporous, and gaseous hydrocarbons; hence the production of *oil-gas* for the purposes of illumination, (p. 494,) and of the several hydrocarbons described by Faraday (p. 483). The old chemists prepared an article which they termed *philosopher's oil*, or *oil of bricks*, by exposing bricks, which had been soaked in oil, to a red-heat in an iron alembic. The products of the destructive distillation of the fixed oils have been principally studied by Bussy and Lecanu. (*Ann. Ch. et Ph.*, xxxi. xxxiii. and xxxiv., and *Journ. de Pharm.*, xi. xii. and xiii.)

The action of air and oxygen on oils has been investigated by Sausure. (*Bibliothèque universelle des Sciences et Arts*, xiii. *Ann. Ch. et Ph.*, xlix. 225.) He found that the recently expressed fixed oils are scarcely affected by the oxygen of the atmosphere; that after a variable period, however, sometimes of several months, but dependent upon temperature and exposure to light, they begin rapidly to absorb oxygen, and evolve carbonic acid and hydrogen. Under certain circumstances these changes may become so rapid as to be attended by inflammation, especially when the surface of the oil is greatly extended, as in the case of greasy cotton, tow, and cloths; and so many cases of spontaneous combustion have arisen from this circumstance, as to render precaution necessary, in shops and in all manufactories and establishments where danger can arise from such causes. (M. HALL, *Quart. Journ. of Science*, v. 367.) The so-called *drying oils* appear to be the most susceptible of this species of oxidizement; they are distinguished from the *fat* or *greasy oils* by drying when exposed in thin layers to the air, into a species of resinous varnish, a property which is accelerated by dissolving in them a very small quantity of oxide of lead. The cause of this property, which is common to nut oil, poppyseed oil, linseed oil, and some others, is not distinctly under-

stood, but is generally ascribed to some peculiarity in their oleine. The greasy oils, under the same circumstances, do not dry, but acquire rancidity, more especially when they contain foreign substances, such as albumine and mucilage. When air is perfectly and entirely excluded, they generally remain without apparent change.

Chlorine, bromine, and iodine, act upon fixed oils so as to form acids with their hydrogen, while compounds of the oil with those halogens are at the same time formed, in which it frequently happens that each atom of the abstracted hydrogen is replaced by an atom of the halogen.

Nitric acid, nitrous acid, and protonitrate of mercury, and in some cases sulphurous acid, convert many of the greasy oils into a concrete fatty matter, which has been termed *Elaidine*, (POUTET, *Ann. Ch. et Ph.*, xii. 58. F. BOUDET, *Ann. Ch. et Ph.*, L. 391, LXIX. 43,) an action which will be afterwards examined. It does not ensue with the drying oils, and has therefore been suggested as a means of detecting the adulteration of olive oil with some of the cheaper oils from seeds, the presence of the latter considerably retarding the solidifying action above adverted to; but the test is equivocal. Sulphuric acid abstracts the glycerine from oils and fats, and produces with it *sulphoglyceric acid*; it also combines with the fatty acids themselves, forming a series of compounds, which have been examined by Fremy, and will again be mentioned. (*Ann. Ch. et Ph.*, LXV. 113.) The action of the alkalis upon oils and fats will also be afterwards adverted to.

The oils when heated with *sulphur* dissolve a portion of that substance, the greater part of which is deposited on cooling; but if the temperature of the oil be raised to what is termed its boiling-point, sulphuretted hydrogen is evolved, and a permanent solution formed. A compound of this kind, obtained by boiling sulphur in linseed oil, has long been known under the name of *balsam of sulphur*; it is dark brown, viscid, and of a disagreeable odor; it requires caution in its preparation on account of its tendency to inflame. This compound is not saponifiable; it mixes with the fat and volatile oils; and when long exposed to the air, dries into an elastic substance, insoluble in ether. When subjected to distillation, sulphuretted hydrogen is produced, together with the usual products of such decomposition, and a black porous mass remains, composed of 45 sulphur, 55 carbon =  $SC_3$ . No sulphuret of carbon is formed. (LÖWIG, ii. 520.) *Selenium* is also dissolved by the fat oils. (BERZELIUS.) *Phosphorus* is sparingly soluble in the fixed oils. 100 parts of olive, or of almond oil, dissolve 2·8 of phosphorus at  $60^\circ$ , and 4 parts at  $212^\circ$ . (BUCHOLZ.) When phosphorus is boiled with the oils, no compound similar to that with sulphur is obtained, nor is any phosphuretted hydrogen evolved. The boiling oils do not dissolve *arsenic*, nor is arsenuretted hydrogen evolved. (REINSCH.) The *chlorides of sulphur, phosphorus, and arsenic* combine with the fixed oils, but the compounds have not been minutely examined. The solubility of these oils in alcohol and in ether is variable. The annexed table shows the relative proportions of carbon, hydrogen, and oxygen contained in 100 parts of each of the following oils, together with the name of the analyst. Some of them yield minute traces of nitrogen, referable to adhering impurities.



|                     | C.    |      | H.    |      | O.    |                         |
|---------------------|-------|------|-------|------|-------|-------------------------|
| Olive oil .....     | 77·21 | .... | 13·36 | .... | 9·43  | Gay Lussac and Thenard. |
| Almond oil .....    | 77·40 | .... | 11·48 | .... | 10·82 | Saussure.               |
| Linseed oil .....   | 76·01 | .... | 11·35 | .... | 12·62 | Ditto.                  |
| Nut oil .....       | 79·77 | .... | 10·57 | .... | 9·12  | Ditto.                  |
| Castor oil .....    | 74·17 | .... | 11·03 | .... | 14·78 | Ditto.                  |
| Whale oil .....     | 76·13 | .... | 12·40 | .... | 11·50 | Bérard.                 |
| Spermaceti oil .... | 78·91 | .... | 10·97 | .... | 10·12 | Ure.                    |
| Hog's-lard.....     | 79·09 | .... | 11·14 | .... | 9·75  | Chevreul.               |
| Suet .....          | 78·99 | .... | 11·70 | .... | 9·30  | Ditto.                  |
| Butter .....        | 65·60 | .... | 17·60 | .... | 16·80 | Bérard.                 |

I shall now enumerate the leading characters of the principal oils and fats of commerce, and then examine the properties of stearine, margarine, and oleine, and of their proximate components, namely, glycerine, and stearic, margaric, and oleic acids. Some peculiar fatty bodies will also be described, together with certain substances allied to this important class of organic products.

### FAT OILS.

1. *Olive oil* is expressed from the pericarp, or fleshy part of the fruit of the *Olea Europæa*, cultivated in France, in Italy, in Spain, and on the coast of Africa. The flavor of the oil varies with the maturity and condition of the fruit; when expressed from immature olives, it is slightly bitter and pungent, and when they are too ripe it is greasy, and tends to rancidity; it has an agreeable flavor of the olive if pressed just before they are fully ripe, but when they are mature the oil is almost tasteless. November and December are the principal harvest months; after that time the olive gradually deteriorates, and yields a very inferior oil. For the best oil, the olives should be gathered by hand, but they are generally beaten off the tree, and if left to ferment, the oil acquires a highly disagreeable smell and taste. What is termed *virgin-oil* is the sweetest, and is obtained by gentle pressure at common temperatures; by stronger pressure and a higher temperature, *common*, or *second oil*, is procured; and a very inferior article is yielded when the husk, after the preceding treatment, is boiled in water. The details of these several operations are described by Dumas (*Chim. App. aux Arts*, vi. 633.)

The finest olive oil is of a pale or greenish-yellow color, a thin consistence, slight odor, and agreeable taste; sometimes it has a nutty flavor, and, when swallowed, leaves a very slight sense of acrimony in the throat. When pure, it has less tendency to change than almost any of the other fat oils; but when of second quality, or carelessly prepared, it soon becomes rancid, and some of the varieties acquire a most repulsive odor and flavor. Its specific gravity at 60° is 0·910; 0·9176, (HEIDENREICH,) 0·9192 at 52°, 0·9109 at 77°, 0·8932 at 122°, and 0·8625 at 200°. (SAUSSURE.) It congeals at 36°, or thereabout.

This oil being less apt than many others to increase in consistence by exposure to air, is preferred for greasing delicate machinery, and especially watch and clock-work. To prepare it for the latter application, the oil is piece of sheet lead, or some shot, are then immersed in it, and it is exposed cooled, and the more liquid portion poured off from the fatty deposit. A

in a corked phial to the action of sunshine. A white matter gradually separates, after which the oil becomes clear and colorless, and is fit for use.

Olive oil is sometimes adulterated with rape or poppy oil, and a method, first suggested by Poutet, (*Ann. Ch. et Ph.*, xii. 58,) is resorted to, to detect the adulteration. A nitrate of mercury is prepared by dissolving 6 parts of mercury in 7.5 parts of nitric acid of sp. gr. 1.36 at common temperature; one part of this solution (which must be used immediately after it is prepared, and not allowed to crystallize,) when added to 10 parts of pure olive oil, forms a mixture which concretes into a hardish mass in the course of a few hours; whereas the admixture of the oil of seeds prevents this induration, so that the resulting mixture is more or less liquid in proportion to the quantity of the seed oil which has been added. Olive oil containing one-twentieth part of poppy oil furnishes in this way a less solid product than when the olive oil is pure; but in order to arrive at satisfactory results, a comparative experiment with mixed oil of known composition should be made at the time. According to Boudet, (*Ann. Ch. et Ph.*, l. 391,) the active agent in Poutet's test is *nitrous acid*, which he therefore proposes to substitute for nitrate of mercury; but Poutet's method is that which has been found most applicable in practice. The indurated fatty matter which is the result of these actions, and which has been termed *Elaidine*, will be described afterwards. (See also, in reference to the detection of adulterations in the fixed oils of commerce, HEIDENREICH, *Chem. Gaz.*, May, 1843, p. 382; and ROUSSEAU'S *Galvanometrical Test*, *Ann. Ch. et Ph.*, xxv. 376.)

2. *Almond oil*, expressed from *sweet* and *bitter almonds* (the kernel or seed of *Amygdalus communis*). The almonds are cleansed, bruised, or coarsely powdered, and pressed in hempen cloths or bags, either between cold or heated iron plates; they yield from 40 to 50 *per cent.* of their weight of a bland oil, which is inodorous whether from sweet or bitter almonds, provided, as respects the latter, that moisture is carefully excluded; if water be present, it acquires the well-known odor evolved on chewing a bitter almond. This oil is very fluid, of a pale yellow, or yellow-green tint, and soon bleaches when exposed to light; it has a slight but agreeable taste; it congeals at about 30°; its sp. gr. at 60° is about 0.918. Its principal use is in pharmacy, as an ingredient in emulsions, and occasionally in liniments, ointments, and soaps. It is soluble in 25 parts of cold, and in 6 of boiling alcohol, and readily dissolves in ether. It soon grows rancid when in contact of air.

3. *Rape oil* is expressed from the seeds of *Brassica rapa* and *Brassica napus*, the former yielding the largest quantity. It is a thick yellow oil, of peculiar taste and smell; it concretes into a yellow mass when cooled to about 28°. Its specific gravity is 0.9167; that from *Brassica napus* being 0.9128 at 60°. It is used in the preparation of woollen goods, and of some kinds of leather, and is much employed in France for burning in lamps; to render it fit for this purpose it is purified by Thenard's process, which consists in agitating it with about a 200th part of sulphuric acid; it is then left at rest for about 24 hours, and two-thirds of its bulk of water, at 165°, are added, the mixture being well stirred or shaken so as to acquire a milky appearance; it is then left at rest for two or three weeks, in a place, the temperature of which is maintained



at about  $80^{\circ}$ , when it clarifies and deposits a dark-colored sediment; it is finally drawn off into vats, the bottoms of which are pierced with holes furnished with filaments of carded wool or cotton, and having been thus filtered, it is fit for use. Sometimes the acid is removed by the addition of powdered chalk. (DUMAS, *Ch. App. aux Arts*, vi. 623.) A superior description of rape oil is known in France under the name of *Colza oil*; it is obtained from the seeds of *Brassica campestris*, which yield about 40 per cent. Its specific gravity is 0.9136 at  $60^{\circ}$ . It may be burned in Argand lamps without previous purification.

4. *Beech-nut oil*. The decorticated nut of the beech-tree (*Fagus sylvatica*), commonly termed *beech-mast*, yields about 15 per cent. of a clear, yellow, inodorous oil by cold, and a larger portion by hot pressure. The remaining cake is a good food for cattle. This oil has a slightly acrid taste, which it loses by keeping, or by boiling it with water. Its sp. gr. at  $60^{\circ}$  is 0.9225. It congeals at  $29^{\circ}$ . It is used in the eastern departments of France for culinary purposes, for burning in lamps, and for the manufacture of soap.

5. *Hazel-nut oil*, extracted, to the amount of 60 per cent., from the kernels of the *Corylus avellana*, is pale, yellow, inodorous, and of a sweetish and agreeable flavor. Its specific gravity is 0.924 at  $60^{\circ}$ . It congeals at about  $30^{\circ}$ .

6. *Oil of Ben* is procured by expression from the decorticated seeds of *Moringa aptera*, a tree resembling a willow, native in Egypt and cultivated at Cairo. This oil is colorless and inodorous; it has an agreeable flavor, and soon after its expression it separates into oleine and margarine: the former is much esteemed for oiling watch and clock work, for it neither becomes viscid nor rancid; hence also its excellence for the preparation of certain scented oils, as of jasmine, tuberose, &c.

7. *Oil of Mustard*. Black and white mustard seeds (*Sinapis nigra* and *Sinapis alba*), yield on pressure a yellow oil, of more consistency than olive oil, nearly inodorous, and of a specific gravity from 0.914 to 0.917. It congeals at about  $30^{\circ}$ . It is applicable to the same uses as rape oil. It is soluble in about 4 parts of ether, and only very sparingly soluble in alcohol. It makes a good soap. Black mustard yields about 18, and white about 36 per cent. of oil.

8. *Alyssum oil* (*Huile de Caméline*), is extracted from the seeds of *Miagram sativum*. It is a yellow oil of a peculiar odor and agreeable taste. Its sp. gr. is 0.925 at  $60^{\circ}$ . It congeals at about  $30^{\circ}$ . According to Dumas this is preferable to rape oil for burning in lamps, but is nevertheless not much used.

9. *Madia oil*. The expressed oil of the seed of *Madia sativa*, a native of South America and California. The oil obtained from this source is said to exceed both in quantity and quality that derived from most other oleiferous plants, and to make a good soap. Some details respecting its culture and produce have been given by Dumas, on the authority of Boussingault. (*Chim. App. aux Arts*, vi. 627.)

#### DRYING OILS.

1. *Linseed oil* is obtained by expression from the ripe seeds of the *Linum usitatissimum*, or common *flax*: they yield from 20 to 25 per cent.

of their weight. When cold-drawn this oil is pale or greenish yellow, but of an amber color or brownish yellow when heat is used, in which case also it is more liable to rancidity; it has a peculiar smell and taste; its sp. gr. is about 0.9395 at 52° (SAUSSURE); it may be cooled down to 4° without at first undergoing any other change than becoming of a paler color, but if kept for some days at that low temperature, it gradually solidifies: when cooled at once down to -17°, it immediately concretes into a yellow mass. It is soluble in 40 parts of cold and 5 of boiling alcohol, and in 1.6 parts of ether.

Linseed oil is extensively used in making paints and varnishes. For these purposes its drying quality is increased by boiling it from three to six hours, and then stirring into it from 7 to 8 hundredths of its weight of litharge, carefully skimming it, and when it has acquired a brownish-red color, withdrawing the fire and leaving it to clarify; it now forms *drying-oil*, or *painter's varnish*. In this operation the lead is partially reduced, and a little oleate and stearate of lead are formed, which are retained in solution in the oil. According to Dr. Thomson, to obtain the best drying oil, every imperial gallon of linseed oil should be boiled with from 2 to 4 ounces of litharge, and half an ounce of sulphate of zinc. When white lead is to be made into a paint with linseed oil, the unboiled oil is preferred in consequence of its paler color. When long kept in a bottle only half filled with it, linseed oil thickens, and then does not dry well, but it is more soluble in alcohol than the fresh oil, and is therefore added with advantage to certain spirit varnishes to diminish their brittleness. (*Org. Chem.* 429.) A mixture of drying oil and mastic varnish is known to artists by the term *Magilp*; it is of a gelatinous consistence, and an excellent vehicle for colors.

Another eminently important use of linseed oil is in the manufacture of *Printing Ink*. The oil is first heated or boiled for some time, and is then set fire to, and after having been suffered to burn for about half an hour, is extinguished by placing a cover upon the vessel, and gently boiled till it acquires a due consistency; in this state it is called *Varnish*, and is viscid, tenacious, and easily miscible with fresh oil or with oil of turpentine, by which it is properly thinned; for common black printers' ink, about a sixth or an eighth part of well calcined lamp black is then added. (For the history of Printers' Ink, see LEWIS, *Philosophical Commerce of the Arts*.)

Silk is often rendered waterproof by the application of successive layers of lithargyrised linseed oil (*oil silk*;) and leather is similarly prepared.

2. *Walnut oil*, obtained by pressure from walnuts (*Juglans regia*), is generally of a pale yellowish-green color, inodorous, and of a peculiar flavor. At about 15° it concretes into a white mass. Its sp. gr. is 0.9283 at 52°; 0.9194 at 76°; 0.874 at 200° (SAUSSURE). When fresh it is sometimes used for culinary purposes, but when rancid it is purgative. It is more drying than even linseed oil, and its want of color renders it a valuable vehicle for many paints. It is sometimes used for burning in lamps, and as an ingredient in certain varnishes.

3. *Hempseed oil* (*Cannabis sativa*.) This is a greenish-yellow oil, of an unpleasant odor and flavor; its sp. gr. is 0.9276 at 52°; at 5° it thickens, and at -17° it freezes. It dissolves abundantly in boiling



alcohol, but cold alcohol retains only about one-thirtieth of its weight in permanent solution. In Russia it is sometimes used for burning, but is apt to form a viscid adherent varnish which clogs the lamp. Its principal consumption is in paint and soap-making.

4. *Poppy oil*, expressed from the seed of the poppy, (*Papaver somniferum*,) is of a very pale yellow color, inodorous, a slight agreeable flavor, and much resembles olive oil, which is sometimes adulterated by it (p. 1253). Its sp. gr. is 0.9249 at 60°. It congeals at 0°. It is soluble in about 25 parts of cold and 6 of boiling alcohol, and dissolves in ether in all proportions. In France and Germany it is frequently used at table as a substitute for olive oil.

5. *Castor oil*. This is the *oleum ricini* of pharmacy, obtained by expression from the seed of the *Ricinus communis*. It has the general characters of a drying oil, but its properties and composition are peculiar. It usually occurs in the form of a thick or viscid oil, often nearly colorless, or only of a pale straw color; it has a slight and peculiar odor, and a bland but somewhat nauseous flavor, followed by a slight degree of acrimony. When cooled down to about 0°, it congeals into a yellow transparent mass. Its sp. gr. is 0.9801 at 49°; 0.9699 at 52°; 0.9575 at 76° (SAUSSURE). It is soluble in all proportions in pure alcohol, so that if mixed with other fixed oils, these may generally be separated from it by the action of alcohol. It is similarly soluble in ether. Its principal use is in medicine, as a mild laxative; it is sometimes employed for certain kinds of printing ink; it is used in perfumery as an application to the hair, and is said to constitute the basis of *Rowland's Macassar oil*. The castor oil formerly employed was expressed with heat, and sometimes boiled out of the seeds, by which a peculiar acrid matter, irritating the eyes and nose, is volatilised, so that cold drawn oil is sometimes regarded as more active than that which has been boiled with water.

The products of the distillation and saponification of castor oil have been specially examined by Bussy and Lecanu, (*Journ. de Pharm.*, xiii. 57,) and the results of the action of nitric acid upon it have been described by Boudet (*Ann. Ch. et Ph.*, L. 41), and by Tilley (*Mem. Chem. Soc.*, i. 1.)

When castor oil is heated in a retort so as to distil over about one-third of it, the residue assumes when cold the appearance of a yellowish porous substance, which requires a high temperature for its decomposition, and is inflammable without undergoing fusion. It is insoluble in water, alcohol, ether, and in the fixed and volatile oils. The alkalis convert it into a species of soluble soap. The distilled liquid includes acetic and *ricinic* acids, and an odorous, colorless, volatile oil, which crystallizes on cooling. (*Stearoricinic* and *Oleoricinic* acids).

*Ricinic acid* is obtained by redistilling the oily liquid after it has deposited the *stearoricinic* acid; the distilled product is *ricinic acid* mixed with some *oleoricinic* acid, but as *ricinic acid* congeals at 50°, the *oleic acid* may be separated from it at or below that temperature, by pressure in bibulous paper, which absorbs the latter and leaves the former in the state of a pearly mass, of an acrid taste. It is fusible at 70° into a colorless oil, and volatile at a little higher temperature. It is insoluble in water, but readily soluble in alcohol and ether, and these solutions redden litmus.

The *ricinates of the alkalis* are soluble in water and in alcohol. *Ricinate of lime*, formed by double decomposition, is insoluble in water and in alcohol. *Ricinate of magnesia* is soluble in alcohol, and forms acicular crystals of a pearly lustre. *Ricinate of lead* is also soluble in alcohol.

According to Bussy and Lecanu, ricinic acid consists of

|                  |    |      |     |      |        | Bussy and Lecanu. |        |
|------------------|----|------|-----|------|--------|-------------------|--------|
| Carbon .....     | 24 | .... | 144 | .... | 73·85  | ....              | 73·56  |
| Hydrogen .....   | 19 | .... | 19  | .... | 9·73   | ....              | 9·86   |
| Oxygen .....     | 4  | .... | 32  | .... | 16·42  | ....              | 16·58  |
| <hr/>            |    |      |     |      |        | <hr/>             |        |
| Ricinic acid.... | 1  |      | 195 |      | 100·00 |                   | 100·00 |

*Oleoricinic acid*. This (which has also been termed *elaiodic acid*) is obtained by boiling the bibulous papers imbued with it, in alcohol; on evaporation the oleoricinic acid remains in the form of a yellow oil of a slight odor and acrid taste. It requires to be cooled considerably below 32° before it congeals. It is insoluble in water, but taken up in all proportions by alcohol.

*Stearoricinic acid*. This is the *margaritic acid* of Bussy and Lecanu, but that term is not sufficiently distinct from *margaric acid*; it is the *Ricintalgsäure* (*Ricinostearic acid*) of Löwig. It is obtained by saponifying 8 parts of castor oil with 2 parts of hydrate of potassa dissolved in 4 parts of water; on heating the mixture it soon forms a viscid transparent soap, completely soluble in water and of a bitter taste. This solution is decomposed by chloride of calcium, and the resulting lime-soap dissolved in boiling alcohol. As this solution cools it deposits a part of the soap; and on filtering, evaporating to dryness, and digesting the residue in ether, a portion of resinous matter, to which the bitterness of the soap appears to be owing, is abstracted, and the rest of the lime-soap remains. When this lime-soap is decomposed by hydrochloric acid, the three fat-acids are separated in the form of a reddish-yellow oil, which, after standing some hours at a temperature between 50° and 60°, deposits stearoricinic acid in a solid state. After pressure between folds of bibulous paper, it may be dissolved in boiling alcohol, and as this solution cools, the pure acid is deposited in the form of pearly scales; it is inodorous and tasteless, insoluble in water, but soluble in half its weight of boiling alcohol, and this solution reddens litmus. It fuses at about 185°, and may be partly distilled without decomposition. With bases it forms compounds resembling the stearates. The formula of this acid appears to be  $C_{22}H_{21}O_3 + HO$ ; its components are

|                          |    |      |     |      |        | Bussy and Lecanu. |        |
|--------------------------|----|------|-----|------|--------|-------------------|--------|
| Carbon .....             | 22 | .... | 132 | .... | 70·91  | ....              | 70·50  |
| Hydrogen .....           | 22 | .... | 22  | .... | 11·83  | ....              | 10·91  |
| Oxygen .....             | 4  | .... | 32  | .... | 17·26  | ....              | 18·59  |
| <hr/>                    |    |      |     |      |        | <hr/>             |        |
| Stearoricinic acid ..... | 1  |      | 186 |      | 100·00 |                   | 100·00 |

*Palmine*\*. This term, having reference to the designation *Palmi Christi* given to the castor oil plant, has been applied by Boudet to the product of the action of nitric or of nitrous acid upon castor oil. This

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\* This must not be confounded with the products of *Palm Oil*.



product is a *palmate of glycerine*. When nitrous acid (or nitrate of mercury, as stated under the head *olive oil*) is made to act upon castor oil, it is converted into a solid wax-like substance; but this change is much less rapid than that which ensues when olive oil is similarly treated; and it deserves notice, that castor oil is the only one of the *drying oils* which is susceptible of this species of solidification.

On adding nitrous acid to castor oil a yellow liquid is at first formed, and the time required for its solidification varies with the quantity of acid employed; when about a twentieth part of acid is used, it solidifies in seven or eight hours, and this, or somewhat less, is the best proportion. If too much acid be used, a third part, for instance, or a half, the temperature rises to  $130^{\circ}$  or  $140^{\circ}$ , effervescence ensues, and the oil becomes opaque, and instead of indurating, remains viscid.

Palmine thus obtained is yellow, but when purified by solution in boiling alcohol, it is white, of a waxy fracture, and requires a temperature of about  $150^{\circ}$  for its fusion. When kept for some months, it occasionally acquires a resinous appearance, and presents an almost vitreous fracture. It has a peculiar odor, appearing to arise from the presence of a volatile oil, and when distilled with water, the distillate has an aromatic odor, but no trace of an essential oil passes over. At the temperature of  $96^{\circ}$  alcohol dissolves about half its weight of palmine; it is much more soluble in boiling alcohol, which, on cooling, deposits it in small opaline, but not crystalline grains. It is very soluble in ether: indeed, when in fusion, ether dissolves it in all proportions.

When palmine is heated in a glass retort, it appears to boil, disengages gases and aqueous vapor, and a peculiar volatile oil passes over, after which the residue suddenly swells up into the neck of the retort, forming a porous resinoid matter resembling that produced during the distillation of castor oil. The volatile oil amounts to about half the weight of the palmine, and when redistilled with water, yields about a third part of an odorous volatile oil, and leaves a more fixed oil which is very acid, soluble in alcohol and in weak solution of potassa, and remains fluid at  $32^{\circ}$ . When this acid oil is triturated with a tenth of its weight of calcined magnesia, the mixture heats and thickens, and ultimately forms a brittle transparent compound, easily soluble in alcohol.

When palmine is boiled in a concentrated solution of potassa, it exhales the characteristic odor of its peculiar volatile oil, and is easily saponified, though less rapidly than castor oil; glycerine is separated, and a saponaceous compound formed, soluble in alcohol and in water. This soap is entirely separable from its aqueous solution by the addition of common salt. When its solution is decomposed at a boiling heat by hydrochloric acid, a peculiar fatty acid separates, which concretes into a crystalline mass on cooling: this is *palmic acid*.

*Palmic acid* forms stellated groups of acicular crystals, fusible at about  $120^{\circ}$ , and very soluble in alcohol and in ether; it reddens litmus, and expels carbonic acid from the carbonates. When heated, a part of it volatilizes without decomposition; a portion of empyreumatic oil is also formed, and carbon remains. The greater number of the *palmates* are soluble in alcohol; *palmate of silver* is insoluble both in water and alcohol, but soluble in ammonia.

*Ænanthylic acid*. (TILLEY, *Mem. Chem. Soc.*, i. 1; *Ann. der Pharm.*,

xxxix., 160.) When castor oil is heated in a retort with twice its weight of nitric acid, previously diluted with its weight of water, a violent action soon commences, and the retort requires for a time to be removed from the sand-heat, when the action gradually subsides; after this a slow distillation may be carried on for some days till the nitrous fumes decrease. In the receiver are found nitric acid, water, and a peculiar oily liquid; and an aqueous liquor and thick fatty matter remain in the retort; the fatty substance may be separated and distilled with some fresh water, and this distillate may be added to the previous product. The volatile oily acid in the receiver is then separated from the water, washed with water, and again distilled with water, and separated as before: it is finally left in contact with anhydrous phosphoric acid, for the purpose of drying it, chloride of calcium not being adapted to the purpose, inasmuch as it is somewhat soluble in the acid.

Ænanthylic acid (so called from being a higher oxide of the radical [ænanthyle] of the *ænanthic acid*, or, as Tilley now proposes to call it, of the *ænanthylous acid*, discovered by Liebig and Pelouze, and which will afterwards be noticed,) is a colorless transparent liquid, of a peculiar aromatic odor, and a pungent taste; it is little soluble in water, but soluble in alcohol and in ether: it burns with a bright flame, and when boiled, suddenly blackens and decomposes, so that it can only be distilled along with water. Its formula is  $C_{14}H_{13}O_3 + HO$ ; the equivalent of the anhydrous acid being 121, that of the hydrated acid, 130. The following are the results of its analysis:—

|                                 |    |     |     |     |        | Tilley. |        |     |        |
|---------------------------------|----|-----|-----|-----|--------|---------|--------|-----|--------|
| Carbon .....                    | 14 | ... | 84  | ... | 65·05  | ...     | 65·34  | ... | 65·33  |
| Hydrogen .....                  | 14 | ... | 14  | ... | 10·63  | ...     | 10·83  | ... | 10·60  |
| Oxygen .....                    | 4  | ... | 32  | ... | 24·32  | ...     | 23·83  | ... | 24·07  |
| Hydrate of œnanthylic acid .... | 1  |     | 130 |     | 100·00 |         | 100·00 |     | 100·00 |

Ænanthylate of baryta,  $C_{14}H_{13}O_3 + BaO$ , is obtained by boiling carbonate of baryta in an alcoholic solution of ænanthylic acid, till it no longer has acid reaction. The hot filtrated solution deposits the salt on cooling in pearly scales, soluble in water and in alcohol, but insoluble in ether: they contain

|                             |   |      |     |      |        | Tilley.    |
|-----------------------------|---|------|-----|------|--------|------------|
| Baryta.....                 | 1 | .... | 77  | .... | 38·88  | .... 38·23 |
| Ænanthylic acid.....        | 1 | .... | 121 | .... | 61·12  | .... 61·77 |
| <hr/>                       |   |      |     |      |        |            |
| Ænanthylate of baryta ..... | 1 |      | 198 |      | 100·00 | 100·00     |

Ænanthylate of silver,  $C_{14}H_{13}O_3 + AgO$ , is prepared by mixing a neutral ænanthylate of ammonia with nitrate of silver; it falls in the form of a white flocculent powder, containing between 48 and 49 *per cent.* of oxide of silver.

6. *Croton oil* is expressed from the seed of the *Croton tiglium*, and is imported from Madras and Bombay. It is a thick brown oil of a peculiar odor, and an acrid taste; a straw-colored oil is also met with, probably from another species of croton. This oil is violently purgative in doses not exceeding even one drop. It consists, according to Nimmo, (*Quart. Journ. of Science*, xviii. 65) of a mixture of an ordinary fat oil, combined with an acrid resin. According to Pelletier and Caventou



(*Journ. de Pharm.*, iv. 289; xi. 10,) the acrid principle of the oil is *crotonine*, and crotonic acid.

*Crotonic acid (Iatrophic acid)* is obtained by saponifying croton oil with potassa, decomposing the soap by tartaric or phosphoric acid, separating the common fat acids, and distilling the remaining liquor; the distillate is then saturated with baryta water, and evaporated to dryness, by which a crotonate of baryta is obtained, and this is decomposed by distillation with phosphoric acid, into a receiver which should be cooled to  $25^{\circ}$  or  $20^{\circ}$ . It is an oleaginous liquid, which congeals at about  $40^{\circ}$ . It is sensibly volatile even below  $32^{\circ}$ , exhaling a nauseous pungent vapor; its taste is acrid, and it is virulently poisonous. (According to Caventou, this acrimony depends upon the presence of another principle.) The *crotonates* are inodorous; *crotonate of potassa* forms prismatic crystals difficultly soluble in alcohol. *Crotonate of baryta* is very soluble both in water and in alcohol. The salts of copper, silver, and lead, occasion white precipitates in a solution of crotonate of ammonia.

#### CONCRETE VEGETABLE OILS. VEGETABLE BUTTERS.

1. *Palm oil*. The sources of this oil are probably several varieties of palms. The *Elais Guineensis*, *Avoira Elais*, and *Cocos Butyracea* are those generally referred to. It has the consistency of soft tallow, or of butter, an orange-yellow color, and an odor which has been compared to that of violets or orris-root. It is lighter than water. It fuses at about  $85^{\circ}$ . It soon grows rancid, becoming at the same time paler colored. It is slightly soluble in cold alcohol; boiling alcohol takes it up more copiously, but deposits the greater part on cooling. It is more soluble in ether.

Palm oil is extensively used in the manufacture of soap and of candles. It admits of bleaching, by the joint agency of air, light, and moisture, at a temperature of  $212^{\circ}$ . (See a description of Spence's process for bleaching palm oil, by Payen, *Ann. Ch. et Ph.*, 1841, ii. 53. Also a paper by Cameron, *Trans. Soc. Arts*, 1833, and by Michaelis, *Poggend. Ann.*, xxvii. 632; and THOMSON'S *Org. Chem.*, 441.) For common soaps the unbleached oil may be used, but for white soap and for candles the bleached oil is employed, though it always retains some color. In candle-making the stearic portion of the oil is used, and it is hardened by the addition of about 5 per cent. of wax; the fusing point of this stearine is about  $120^{\circ}$ , and the average proportion of the stearine to the elaine of the original oil is about 30 to 70. The palm elaine remains liquid at  $60^{\circ}$ , and is easily saponifiable. According to Stenhouse and Fremy (*Ann. der Pharm.*, xxxvi. 44,) common palm oil contains margarine and oleine, and a peculiar fat termed *Palmitine*, and in old oil there is often a large proportion of free palmitic acid.

*Palmitic or Palmatylic acid* (not to be confounded with the *palmic acid of castor oil*, above described) is obtained by saponifying palm oil, and especially the old oil, with caustic soda, and decomposing the resulting soap by hydrochloric or tartaric acid. The mixed fatty acids which are thus set free are to be dissolved in boiling alcohol, and on cooling the palmitic acid separates; it must be purified by pressure in

bibulous paper, and repeated crystallization. It is a beautiful white substance, sparingly soluble in cold, but abundantly in hot alcohol, and this solution reddens litmus. It fuses at about  $140^{\circ}$ . The components of *anhydrous palmitic acid* (which has not been isolated) are

|                               |    |      |     |      |        |
|-------------------------------|----|------|-----|------|--------|
| Carbon .....                  | 32 | .... | 192 | .... | 77.94  |
| Hydrogen .....                | 31 | .... | 31  | .... | 12.42  |
| Oxygen .....                  | 3  | .... | 24  | .... | 9.64   |
| <hr/>                         |    |      |     |      |        |
| Anhydrous palmitic acid ..... | 1  |      | 247 |      | 100.00 |

The ordinary acid is  $C_{32}H_{31}O_3 + HO$ , and has been analyzed by Fremy, Stenhouse, and Sthamer, with the following results:—

|                        |    |     |     |     |        | Stenhouse. |        | Fremy. |       | Sthamer. |       |
|------------------------|----|-----|-----|-----|--------|------------|--------|--------|-------|----------|-------|
| Carbon .....           | 32 | ... | 192 | ... | 75.00  | ...        | 75.69  | ...    | 75.1  | ...      | 75.20 |
| Hydrogen .....         | 32 | ... | 32  | ... | 12.50  | ...        | 12.11  | ...    | 12.4  | ...      | 12.67 |
| Oxygen .....           | 4  | ... | 32  | ... | 12.50  | ...        | 12.20  | ...    | 12.5  | ...      | 12.13 |
| <hr/>                  |    |     |     |     |        |            |        |        |       |          |       |
| Hydrated palmitic acid | 1  |     | 256 |     | 100.00 |            | 100.00 |        | 100.0 |          | 100.0 |

The palmitic acid analysed by Sthamer was obtained by the saponification of the substance known as *Japan wax* (the produce of the *Rhus succedaneum*,) and which he found to be a *palmitate of glycerine* (*Ann. der Pharm.*, xliii., 335.)

At common temperatures chlorine has no action on palmitic acid, but at  $212^{\circ}$  it forms several combinations by the displacement of equivalent atoms of hydrogen. The most stable of these compounds appears to be  $C_{32}H_{28}O_4Cl_4$ ; they all act as acids.

*Palmitate of ammonia* is insoluble in cold water. (FREMY.) *Palmitate of soda* may be obtained in crystals by the slow evaporation of its dilute alcoholic solution. (STHAMER.) *Palmitate of silver*  $= AgO + C_{32}H_{31}O_3$ , falls in the form of a bulky precipitate on adding a dilute alcoholic solution of palmitate of soda to a neutral nitrate of silver: dried at  $32^{\circ}$ , it consists of

|                          |   |      |     |      |        |       | Sthamer. |      | Stenhouse. |
|--------------------------|---|------|-----|------|--------|-------|----------|------|------------|
| Oxide of silver .....    | 1 | .... | 116 | ...  | 31.96  | ....  | 31.95    | .... | 31.45      |
| Palmitic acid .....      | 1 | .... | 247 | .... | 68.04  | ....  | 68.05    | .... | 68.55      |
| <hr/>                    |   |      |     |      |        | <hr/> |          |      |            |
| Palmitate of silver..... | 1 |      | 363 |      | 100.00 |       | 100.00   |      | 100.00     |

2. *Coco-nut Oil*. The oil of the common coco-nut (*Cocos nucifera*.) At temperatures below  $70^{\circ}$  or  $71^{\circ}$  this oil is concrete; at  $74^{\circ}$  or  $75^{\circ}$  it is fluid. Its stearine and elaine may to a certain extent be separated by pressure at proper temperatures. The stearine has been used for the manufacture of candles, but its point of fusion is too low to render it conveniently applicable for that purpose, as in crowded and hot places, or at a high summer temperature, they would be apt to soften and even run down: mixed with the stearic acid of tallow, coco-stearine yields a good candle at a low price. *Price's composite candles* consist of such a mixture: their fusing point is about  $112^{\circ}$  or  $113^{\circ}$ , and may be heightened by the further addition of tallow-stearic acid, the fusing point of which is  $131^{\circ}$ . The elaine of coco-nut oil, which remains liquid at common temperatures, cannot be conveniently burned in an Argand lamp of the ordinary construction, in consequence of its charring in the wick; with a view to cheapness, and to combustion in what is termed the *solar-*



*lamp*, it may be mixed with spermaceti oil, but the latter is deteriorated in proportion to such addition.

The stearine of coco-nut oil, which has been designated *cocinine*, is, according to Bromeis, (*Ann. der Pharm.*, xxxv. 277,) a combination of glycerine with a peculiar fat acid, the *cocostearic* or *cocinic acid*. To prepare it, the coco-nut oil is saponified by boiling with caustic potassa, and the resulting soap decomposed by hydrochloric acid, so as to separate the fat acids; these are subjected to pressure to get rid as far as possible of oleic acid, and then again saponified and decomposed as before; the resulting cocinic acid is purified by solution and crystallisation in alcohol. It is white, inodorous, hard, and brittle, and almost transparent at the edges. According to Bromeis, it fuses at  $95^{\circ}$ , but according to Brandes at about  $80^{\circ}$ . At first it appears to have little taste, but is afterwards slightly acrid; it is insoluble in water, but soluble in all proportions in absolute alcohol and in ether. Common spirit of wine scarcely dissolves it. Heated with a solution of common salt, it may be almost entirely sublimed. The formula of the *anhydrous acid*, which however has not been isolated, is  $C_{26}H_{25}O_3$ , and its equivalent 205; the *hydrated acid* is  $C_{26}H_{25}O_3 + HO$ , or

|                             |    |     |     |     |        | Bromeis. |
|-----------------------------|----|-----|-----|-----|--------|----------|
| Carbon .....                | 26 | ... | 156 | ... | 72.80  | 72.82    |
| Hydrogen .....              | 26 | ... | 26  | ... | 12.14  | 12.23    |
| Oxygen .....                | 4  | ... | 32  | ... | 15.06  | 14.95    |
| <hr/>                       |    |     |     |     |        |          |
| Hydrated cocinic acid ..... | 1  |     | 214 |     | 100.00 | 100.00   |

According to St. Evre (*Ann. Ch. et Ph.*, 3me Ser. xx. 100,) the anhydrous cocinic acid is represented by the formula  $C_{22}O_{22}O_4$ .

The *cocinales* have been examined by Bromeis and by Brandes, but according to Löwig, (*Chem. der Org. verb.*) the acid employed by the latter was impure. *Cocinate of silver*, obtained by decomposing nitrate of silver by a solution of cocinate of soda, consists, according to Bromeis, of

|                         |   |     |     |     |        |
|-------------------------|---|-----|-----|-----|--------|
| Oxide of silver .....   | 1 | ... | 116 | ... | 36.13  |
| Cocinic acid .....      | 1 | ... | 205 | ... | 63.87  |
| <hr/>                   |   |     |     |     |        |
| Cocinate of silver..... |   |     | 321 |     | 100.00 |

3. *Chocolate nut-oil* is expressed from the seed of the *Theobroma Cacao*, a lofty tree, native in South America. It is of the consistence of tallow, of a yellowish color, and rather agreeable flavor, and not prone to rancidity: its sp. gr. is 0.91: it fuses at about  $120^{\circ}$ . It is this fat which gives greasiness to *chocolate*; which is made by torrefying the chocolate beans, and rubbing or grinding them into a fine paste in a hot mortar: sugar and aromatics are frequently added.

4. *Nutmeg Butter. Expressed Oil of Nutmeg.* (The concrete oil of the *Myristica moschata*.) This substance is prepared in Holland; the nutmegs are beaten to a paste, which is inclosed in a bag, steamed, and pressed between hot plates. It is imported in oblong cakes of the shape of a small brick, wrapped in flag leaves. It is usually of an orange or reddish-brown color, and of a fragrant odor. According to Playfair, (*Ann. der Pharm.*, xxxvii. 152,) nutmeg butter consists of three fatty substances, two of which are soluble, but the third nearly

insoluble in common alcohol; this latter has been termed *Myristine*; when purified by repeated washing in alcohol or ether, and pressure in bibulous paper, it may be rendered nearly colorless and inodorous, and is then a compound of glycerine with *myristic acid*. (See also BOLLAERT, *Quart. Journ. of Science*, xviii. 317.)

*Myristic acid* is obtained by boiling myristine in a concentrated solution of caustic potassa, which forms with it a viscid soap; this, dissolved in boiling water, and decomposed by hydrochloric acid, yields the myristic acid in the form of a colorless oil, which concretes into a crystalline mass on cooling. It is very soluble in boiling alcohol, but the greater part separates as the solution cools. It is sparingly soluble in cold ether, and very soluble in boiling ether; it is insoluble in water. It fuses at  $120^{\circ}$ . In its anhydrous state, as existing in the myristates, its formula is  $C_{28}H_{27}O_3$ , and its equivalent 219. The crystallized acid is  $C_{28}H_{27}O_3 + HO$ , or

|                             |    |     |     |     |        | Playfair. |        |
|-----------------------------|----|-----|-----|-----|--------|-----------|--------|
| Carbon .....                | 28 | ... | 168 | ... | 74.06  | ...       | 74.12  |
| Hydrogen .....              | 28 | ... | 28  | ... | 12.09  | ...       | 12.31  |
| Oxygen .....                | 4  | ... | 32  | ... | 13.85  | ...       | 13.57  |
| <hr/>                       |    |     |     |     |        |           |        |
| Hydrated myristic acid..... | 1  |     | 228 |     | 100.00 |           | 100.00 |

*Myristate of potassa*,  $KO + C_{28}H_{27}O_3$ , is a white crystallisable salt, soluble in water and in alcohol, but not in ether. It is formed by digesting the acid in a strong solution of carbonate of potassa, evaporating to dryness, and dissolving the salt in alcohol. *Myristate of baryta* falls as a white precipitate on adding myristate of potassa to chloride of barium. It contains between 25 and 26 *per cent.* of baryta, being  $BaO + C_{28}H_{27}O_3$ . The *myristate of lead*, and of *silver*, have also been described by Playfair.

5. *Laurel Butter*. The expressed oil of the berries of the *Laurus nobilis*. According to Sthamer, the same oil is obtained from the berries of the *Laurus Pichurim*, originally examined by Bonastre, (*Journ. de Pharm.*, xi. 1.) This is a greenish oil, of the consistency of butter, and of a peculiar odor. It fuses at about  $100^{\circ}$ . The stearine of this oil (which according to Marsson, *Ann. der Pharm.*, xli. 329, is a *Laurostearate of Glycerine*) yields, when its potassa soap is decomposed in boiling water by tartaric acid, an oily matter which concretes on cooling, and which is *Laurostearic acid*. It is soluble in alcohol and ether. Its formula is  $C_{24}H_{23}O_3 + HO$ .

#### ANIMAL FATS AND OILS.

These constitute a numerous and important series of compounds, some of which are solid and others liquid, at ordinary temperatures. There are two opinions respecting the origin of fat in animals. Liebig (*Animal Chemistry applied to Physiology, &c.*) endeavours to show that sugar, starch, and other non-azotised articles of food are the sources of fat in animals, and that they are convertible into fat by a process of deoxidizement, "that by the mere separation of a part of their oxygen, they may pass into fat, or at least into a substance having exactly the composition of fat. If from the formula of starch,  $C_{12}H_{10}O_{10}$ , we take 9 equivalents of oxygen, there will remain  $C_{12}H_{10}O$ .



The empirical formula of fat which comes nearest to this, is  $C_{11}H_{10}O$ ; according to which, an equivalent of starch, in order to be changed into fat, would lose 1 equivalent of carbonic acid  $CO_2$ , and 7 equivalents of oxygen, &c." Dumas, on the contrary, attributes the power of *forming fat* exclusively to the vegetable kingdom. "Les animaux ne forment pas de graisse; les plantes seules ont ce privilège." But animals accumulate and modify the fat which is originally formed by vegetables; and hence the fat of herbivora is that which most closely resembles the fat of the alimentary vegetables, and the fat of carnivora that which has undergone the greatest modification. These questions, however, are of too complicated a character to be further discussed in this place.

It has already been stated, that animal fat is contained in what is termed *adipose membrane* or cellular tissue; that it may be obtained by exposure to a heat sufficient to liquify the fat and burst its including cells; and this should be done before any putrefaction of the membrane, or of the blood, fibre, and other accidentally adhering matters has taken place. To facilitate the operation, the fat should be chopped up into small pieces, so as to allow of the more uniform influence of heat. The remaining membranes are rendered crisp by the heat, and when the fat has been entirely pressed out of them, are sold in the form of flat cakes called *greaves* or *cracklings*, used as food for dogs, as manure, and in the manufacture of ferrocyanide of potassium.

1. *Mutton Suet*. The fat of sheep is white, and has little odor when fresh, but acquires a peculiar rancid smell when exposed for some time to air. Its point of fusion lies between  $100^{\circ}$  and  $106^{\circ}$ . It dissolves in about 45 parts of boiling alcohol, of sp. gr. 0.820, and on cooling, stearine is deposited. The stearine of mutton suet is white and without lustre; when it has been fused it begins to concrete at  $100^{\circ}$ , and the temperature then rises to  $111^{\circ}$ . The oleine of this fat is colorless, and has a slight odor derived from the presence of *hircine*.

2. *Beef Fat*. The fat of oxen is yellowish-white, and has a peculiar odor; it fuses at about  $100^{\circ}$ , and is dissolved by about 40 parts of boiling alcohol. It contains about three-fourths its weight of stearine, which is white, granular, and crystalline; when fused it may be cooled down to  $102^{\circ}$  before it begins to congeal, and the temperature then rises to  $111^{\circ}$ ; 100 parts of boiling absolute alcohol dissolve between 15 and 16 of this stearine.

To separate the stearine and oleine of *tallow*, the fat is melted and incessantly stirred whilst in the act of congelation. It is then pressed in woollen bags at a temperature of about  $95^{\circ}$ ; the elaine which is thus squeezed out still retains much stearine, it is therefore cooled down to about  $90^{\circ}$ , and again pressed, and these successive coolings and pressings are repeated, sinking the temperature each time by a few degrees, till at last an elaine is obtained, which remains liquid at  $32^{\circ}$ , and the stearine is hard and granular.

There is an article known in trade under the name of *Neat's foot oil*; it is obtained from the feet of oxen; the hair and hoofs are removed, and the bone rasped down, is boiled in water with the surrounding parts, when the oil separates and floats upon the surface. This oil is not liable to change or rancidity, and remains liquid below  $32^{\circ}$ ; it is used for greasing machinery, and more especially for steeple clocks, which require,

in consequence of the cold to which they are frequently exposed, an oil not liable to solidify.

3. *Hog's Lard*. This is a white inodorous soft fat, the fusibility of which fluctuates between  $80^{\circ}$  and  $88^{\circ}$ . Its sp. gr. at  $60^{\circ}$  is 0.9302; at  $102^{\circ}$ , 0.9028; at  $122^{\circ}$ , 0.8918; at  $156^{\circ}$ , 0.8811; at  $200^{\circ}$ , 0.8628. (SAUSSURE.) When subjected to repeated and powerful pressure between bibulous paper, it is separated into 38 parts of granular stearine, the fusing point of which is about  $110^{\circ}$ , and which has been used for the manufacture of candles; and 62 of elaine; the latter forms a good substitute for spermaceti and other more expensive oils, employed in lubricating machinery. When hog's lard is long exposed to air, it grows yellow, rancid, and sour, a volatile fatty acid being developed, which Chevreul considers analogous to the *caproic acid*. By the action of nitric acid hog's lard is converted into margaric and oleic acid. (BUSSY and LECANU, *Journ. de Pharm.*, xii. 605.)

4. *Horse Fat* is almost liquid at  $60^{\circ}$ ; it has a disagreeable odor.

5. *Goat's Fat* is characterized by its disagreeable capreous odor, arising from its containing a peculiar fat, which Chevreul has termed *hircine*, and which, on the separation of its tallow into stearine and elaine, accompanies the latter, and cannot be perfectly separated from it. During the saponification of its elaine, *hircic acid*, of a strong goaty odor, is formed: this acid may be obtained by saponifying 4 parts of goat fat with 1 of hydrate of potassa and 4 of water, diluting the soap with more water, and decomposing it by phosphoric or tartaric acid, washing the evolved fat acids, and distilling the sour water and washings; if a drop of the distilled product, evaporated upon a platinum leaf, leaves any residue, it must be redistilled; the product is then to be saturated by hydrated baryta, evaporated to dryness, and decomposed by distillation with equal parts of sulphuric acid and water: *hircic acid* then passes over in the form of a colorless volatile oil.

*Hircic acid* has a capreous and acetic odor, reddens litmus, and dissolves difficultly in water, and easily in alcohol. It forms distinct salts with the bases; *hircate of ammonia* is peculiarly odorous; *hircate of potassa* is deliquescent; *hircate of baryta* is difficultly soluble.

6. *Hare's Fat* is reddish-yellow and unctuous; it has some of the properties of the drying oils.

7. *Human Fat* is soft, yellowish, inodorous, and varies a little in different parts of the body; that from the region of the kidneys, when fused, begins to concrete at  $76^{\circ}$ , and is solid at  $64^{\circ}$ . It is soluble in 40 parts of boiling alcohol of 0.821, and on cooling, the solution deposits *stearine*, which, after having been pressed between folds of blotting paper at  $78^{\circ}$ , is colorless, fusible at  $122^{\circ}$ , and may be cooled to  $106^{\circ}$  before it begins to congeal; its temperature then rises to  $120^{\circ}$  from the evolution of latent heat. 100 parts of boiling anhydrous alcohol dissolve 21.5 of this stearine, of which the greater part separates, on cooling, in acicular crystals. The *elaine* of human fat is a colorless, inodorous oil, which retains its fluidity at  $40^{\circ}$ ; its specific gravity is 0.913 at  $60^{\circ}$ ; it has a sweetish taste. 100 parts of boiling alcohol dissolve 123 of this elaine, and the solution becomes turbid when it has cooled to  $170^{\circ}$ .

Under the name of *Adipocire*, Fourcroy described a peculiar fatty matter found in a cemetery in Paris, and supposed to have been partly



formed during putrefaction. Similar collections of fatty matter are found in the pits which collect the offal of dissecting-rooms and slaughter-houses, and the same kind of fatty matter remains when the bodies of animals are exposed to running water till the muscular and membranous parts have been washed away. Chevreul has shown that this substance is the original fat of the body, which has resisted decomposition, and is partly in the state of fatty acid and partly saturated by ammonia, with traces of lime and magnesia.

8. *Fat of Birds.* *Goose Fat* is colorless and of a peculiar taste and odor. When fused it congeals at  $80^{\circ}$  into a buttery consistence; subjected to pressure at  $30^{\circ}$ , it yields 68 elaine and 32 stearine, fusible at  $112^{\circ}$ . *Duck Fat* fuses at  $76^{\circ}$ , and yields 72 elaine and 28 stearine, fusible at  $120^{\circ}$ . *Turkey Fat* yields 74 elaine and 26 stearine, fusible at  $112^{\circ}$ . (BRACONNOT.)

9. *Train Oil.* *Whale Oil.* Common *whale oil* has a specific gravity  $= 0.927$  at  $68^{\circ}$ ; at  $32^{\circ}$  it deposits *stearine*, and the remaining *oil* is then soluble in 0.82 of its weight of absolute alcohol at  $168^{\circ}$ . It is easily saponified, yielding a brown soluble soap, which, decomposed by tartaric acid, affords fat acids and glycerine, together with traces of *phocenic acid*. The *stearine* of train oil congeals, after fusion, at between  $70^{\circ}$  and  $80^{\circ}$ . It dissolves in 1.8 parts of boiling anhydrous alcohol, from which it crystallizes, on cooling, leaving a brown mother liquor.

10. *Spermaceti Oil.* *Spermaceti.* *Cetine.* *Ethal.* *Cetene.* The oil of the spermaceti whale is more pure, and burns more perfectly and more brilliantly in lamps than common whale oil; it deposits, as it cools after the death of the animal, a crystalline fatty substance, called *spermaceti*. The specific gravity of spermaceti oil is about 0.927. It is easily saponified, furnishing a brown soluble soap.

*Spermaceti* is purified by pressure, and boiling in weak solution of potassa; it is then washed, fused in boiling water, and cast into blocks or cakes, which exhibit a beautiful lamellar crystalline texture, especially when the interior liquid part is suffered to run out of the exterior concrete case. It has a greasy feel. Its specific gravity is about 0.94; it fuses at  $112^{\circ}$ . 100 parts of boiling alcohol of 0.821 dissolve 3.5 parts, of which 0.9 fall on cooling. Its solution in hot ether congeals on cooling. It dissolves in the hot oils. When common spermaceti is triturated with alcohol, a little oily matter is abstracted, and when the whole of this is removed, the residuary pure spermaceti has been termed by Chevreul *cetine*.

*Cetine*,  $C_{208}H_{208}O_{16}$ , fuses at  $120^{\circ}$ . 100 parts of boiling absolute alcohol dissolve 15.8 of cetine, but alcohol of 0.831, only 3 parts; the greater part separates on cooling in pearly scales. Acids act upon it as on other fats. It is difficultly saponifiable by the hydrated alkalis. Digested for several days between  $120^{\circ}$  and  $190^{\circ}$ , with a solution of caustic potassa, in twice its weight of water, it is at length converted into a peculiar soap, containing margarate and oleate of potassa, together with an unsaponified fat, which Chevreul terms *ethal*. On decomposing this soap by an acid, ethal, and oleic and margaric acids separate, amounting together to 101.6 parts from 100 of cetine; of this 60.96 parts consist of fat acids, and 40.64 of ethal: no glycerine is produced, but 0.9 of a yellowish extractive matter; nor is any volatile acid formed.

Chevreul, Saussure, and Berard have analyzed cetine and ordinary spermaceti, and Dr. Ure spermaceti oil, with the following results :

|                | <i>Cetine.</i><br>Chevreul. |      | <i>Spermaceti.</i><br>Berard. |      | <i>Spermaceti.</i><br>De Saussure. |      | <i>Spermaceti Oil.</i><br>Ure. |
|----------------|-----------------------------|------|-------------------------------|------|------------------------------------|------|--------------------------------|
| Carbon .....   | 81.660                      | .... | 79.5                          | .... | 75.474                             | .... | 78.00                          |
| Hydrogen ..... | 12.862                      | .... | 11.6                          | .... | 12.795                             | .... | 11.80                          |
| Oxygen .....   | 5.478                       | .... | 8.9                           | .... | 11.377                             | .... | 10.20                          |

In reference to its atomic composition, cetine has been regarded as consisting of

|                |     |      |      |      |        |
|----------------|-----|------|------|------|--------|
| Carbon .....   | 208 | .... | 1248 | .... | 78.78  |
| Hydrogen ..... | 208 | .... | 208  | .... | 13.13  |
| Oxygen .....   | 16  | .... | 128  | .... | 8.09   |
| <hr/>          |     |      |      |      |        |
| Cetine .....   | 1   |      | 1584 |      | 100.00 |

*Ethal*,  $C_{32}H_{33}O, HO$ , is obtained by saturating the fat acids resulting from the decomposition of spermaceti soap, with hydrated baryta, washing away all excess of baryta, drying the residue, and digesting it in cold alcohol or ether, which dissolves the ethal and leaves a barytic soap. The ethal remains, on distilling off the alcohol, in the form of a solid transparent crystalline fat. Ethal may also be obtained by adding 1 part of caustic potassa, in small fragments, to 2 parts of fused spermaceti, and stirring the mixture till the combination is complete; a solid soap is thus formed, which may be decomposed by slight excess of hydrochloric acid, when the ethal and free acids separate, and form, when gently heated, an oily layer upon the surface, which is to be poured off and again saponified, (in order effectually to decompose all remaining spermaceti,) decomposed by hydrochloric acid as before, and the ethal and acids poured off and mixed with excess of slaked quicklime: the mixture of calcareous soaps and ethal thus obtained is digested in alcohol, which takes up the ethal and leaves it on distillation: it may be finally purified by solution in ether, and subsequent evaporation of the solvent. It is tasteless and inodorous, and concretes, when fused alone, at  $118^{\circ}$ , but if fused with water, at  $124^{\circ}$ . It is volatile when distilled either alone or with water, and in this way it may be purified; it burns like wax. It dissolves in all proportions in alcohol of 0.812 at  $128^{\circ}$ , and separates, on cooling, in lamellar crystals. It is decomposed when heated with sulphuric and nitric acid. It does not combine, at common temperatures, with caustic potassa, when pure, but when mixed with soap it forms a milky fluid, which leaves, upon a filter, a mixture of ethal with margarate and oleate of potassa, exactly resembling hydrated alumina. The results of the mutual action of ethal and sulphuret of carbon have been examined by Provostaye and Desains. (*Ann. Ch. et Ph.*, Dec., 1842.)

Ethal is regarded as the hydrated oxide of *Cetylle*, a hypothetical radical =  $C_{32}H_{33}$ . Its ultimate elements are

|                |    |      |     |      | Chevreul. |
|----------------|----|------|-----|------|-----------|
| Carbon .....   | 32 | .... | 192 | .... | 79.34     |
| Hydrogen ..... | 34 | .... | 34  | .... | 14.05     |
| Oxygen .....   | 2  | .... | 16  | .... | 6.61      |
| <hr/>          |    |      |     |      |           |
| Ethal .....    | 1  |      | 242 |      | 100.00    |



These elements, as the term *ethal* implies, will be found to bear a relation to the elementary composition of ether and alcohol, for if ether be regarded as  $= C_4H_4 + HO$ , alcohol will be  $C_4H_4 + 2HO$ , and ethal  $= C_{32}H_{32} + 2HO$ .

If, with Dumas and Peligot (*Ann. Ch. et Ph.*, LXII. 1), spermaceti or cetine be regarded as an oleo-margarate of ethal, its constituents will be

|                       |   |
|-----------------------|---|
| 2 Margaric acid ..... | C <sub>68</sub> H <sub>66</sub> O <sub>6</sub>    |
| 1 Oleic acid .....    | C <sub>44</sub> H <sub>40</sub> O <sub>4</sub>    |
| 3 Ethal.....          | C <sub>96</sub> H <sub>102</sub> O <sub>6</sub>   |
| <hr/>                 |   |
| 1 Cetine .....        | C <sub>208</sub> H <sub>208</sub> O <sub>16</sub> |

But according to L. Smith (*Ann. Ch. et Ph.*, 3me Ser. VI., 40, Sept., 1842), pure spermaceti (cetine) contains neither oleic nor margaric acid, but the product of its saponification is exclusively *ethalic acid*; he therefore regards spermaceti as an *ethalate of ethal*. When pure cetine is heated in a retort to the boiling-point of mercury, a substance slowly passes over and concretes, which is no longer cetine, being more fusible, strongly reddening litmus, and having a peculiar odor (not however due to acroleine, which is only formed when the cetine is impure). This product, according to Smith, is a mixture of *cetene* (hydrocarbon) and ethalic acid.

*Cetene*. By distilling ethal with pure phosphoric acid, Dumas and Peligot succeeded in abstracting its water, and obtaining its hydrocarbon in a free state; it passed over in the form of an oily liquid, more volatile than ethal, and yielding a vapor of the density of 7.846, whence they infer that it is a distinct form of hydrocarbon  $= C_{32}H_{32}$ . To this compound they have given the name of *Cetene* (*Ann. Ch. et Ph.*, LXII. 1) and ethal, as above represented, would be a *binhydrate of cetene*.

Cetene is a colorless, tasteless liquid, leaving a greasy stain on paper, and of an oily aspect; it boils at 528° (275° Cent.), and distils unaltered; it is insoluble in water, very soluble in alcohol and ether, and inactive upon test papers. It burns with a pure white flame. As it does not congeal, and is apparently unchanged by exposure to air, it would probably furnish a valuable substitute for oil, as applied to watches and clocks.

*Sulphocetic Acid*. When ethal and sulphuric acid are heated in a water bath, they combine, and on dissolving the product in alcohol and saturating the solution with an alcoholic solution of potassa, sulphate of potassa is deposited, and *sulphocetate of potassa* and ethal remain dissolved: on filtering and evaporating the liquid, crystals are obtained, which must be redissolved in absolute alcohol to separate adhering sulphate of potassa, and recrystallized: this product is then triturated with sulphuric ether, to remove any remaining ethal, and pure sulphocetate of potassa remains. It is a white nacreous salt.

11. *Porpoise Oil*. The oil of the *Delphinus phocaena*, and *Delphinus globiceps*, has been examined by Chevreul. When saponified, it yields a peculiar fat-acid, which has been termed *phocenic*, or *delphinic acid*. This acid is best obtained from that portion of porpoise oil which remains dissolved in cold alcohol of 0.825. It is saponified, and a *phocenate of baryta* formed, 100 parts of which are decomposed by 205 of

phosphoric acid, of 1.12 specific gravity, or by 23.4 parts of sulphuric acid, diluted with twice its weight of water, when nearly the whole of the phocenic acid separates. This acid exists in spermaceti, and in the berries of the *Viburnum opulus*.

*Phocenic acid*,  $C_{10}H_7O_3, HO$ , resembles a volatile oil, retaining its fluidity at  $15^\circ$ ; although its boiling-point is above  $212^\circ$ , it volatilizes in the air; it has a rank and acetic odor and acrid taste. Its specific gravity is 0.932 at  $77^\circ$ ; water at  $88^\circ$  only dissolves an eighteenth part of its weight; alcohol of 0.795 takes it up in all proportions. Anhydrous phocenic acid consists, according to Chevreul's analysis, of

|                               |    |      |    |      |        |
|-------------------------------|----|------|----|------|--------|
| Carbon .....                  | 10 | .... | 60 | .... | 65.93  |
| Hydrogen .....                | 7  | .... | 7  | .... | 7.69   |
| Oxygen .....                  | 3  | .... | 24 | .... | 26.38  |
| <hr/>                         |    |      |    |      |        |
| Anhydrous phocenic acid ..... | 1  |      | 91 |      | 100.00 |

When the *phocenates* are heated, they exhale an aromatic odor, and yield, on distillation, an oily liquid, insoluble in potassa. The *phocenates of potassa, soda, and strontia* are deliquescent; *phocenate of baryta* yields efflorescent crystals, soluble in their weight of water. *Phocenate of lead* is soluble, but during the evaporation of its solution, passes into a difficultly-soluble subsalt.

*Phocenine* is the term applied by Chevreul to that part of the oil which yields phocenic acid, and which is separated by boiling alcohol, from the common fats.

12. *Cod Liver Oil. Oleum jecoris aselli.* The liver of the *Morrhua vulgaris*, or common cod fish, abounds in oil, which is obtained by expression and by boiling; it has lately been much used in medicine as an alterative: its efficacy has been ascribed by some to the presence in it of iodine, by others to bromine; as it occurs in commerce, it varies in color from pale yellow to dark yellow and reddish-brown. The presence of iodine may be detected in it by saponifying it with potassa, neutralising by dilute sulphuric acid, separating the fat acids, and slowly evaporating the sulphuric solution, which furnishes crystals of sulphate of potassa, and in the mother-liquor iodine may be detected by adding solution of starch with chlorine or dilute nitric acid. (LIEBIG, *Chim. Org.* ii. 283.) The oil of the liver of the *skate* is also said to contain iodine. (*Chem. Gaz.*, Mar. and Apr., 1843.)

13. FAT OF INSECTS. Many insects contain more or less fat, but its peculiarities have been but little examined. The fatty matter of *cochineal* (*Coccus cacti*) has been examined by Pelletier and Caventou. (*Ann. Ch. et Ph.*, viii. 271.) It is obtained by digesting cochineal in ether, evaporating, and dissolving the residue in hot anhydrous alcohol, which, on cooling, deposits the fat; this solution must be repeated till it is colorless. The fat of the *Coccus polonicus* crystallizes like spermaceti. *Cantharides* also contain a fatty matter, and an acrid principle, or *cantharidine*. If the watery extract of these insects be digested in alcohol, a tincture is obtained, which, by slow evaporation, yields a resinous residue; if this be digested in ether, it forms a yellow solution; by spontaneous evaporation it deposits crystalline plates, which may be



freed from some adhering color by alcohol; they resemble spermaceti in appearance, and are soluble in boiling alcohol, but precipitate as it cools. They are insoluble in water. Besides this peculiar principle, cantharides contain a green inert oil, soluble in alcohol; a black matter, insoluble in alcohol, but soluble in water: a yellow substance, soluble in both; a considerable portion of uric acid; a little acetic acid; and phosphates of lime and magnesia.

14. *Butter.* (See *Milk.*)

15. *Wax.* Much difference exists in the statements of different chemists respecting the proximate and ultimate composition of wax. The opinions, too, respecting its origin are much at variance, some supposing that the bees form wax out of honey, (LIEBIG, *Mem. Chem. Soc.*, i. 165), others, that they merely collect it, and that its formation is exclusively a process of vegetable life. (DUMAS, BOUSSINGAULT, and PAYEN, *Ann. Ch. et Ph.*, 3me Series, iv. 208.) In short, the same arguments have been adduced in favor of these opinions, as in respect to the formation of fat in general. But Huber long ago endeavoured to show that the bee has the power of forming wax when fed only upon honey, (*Obs. sur les Abeilles*,) and the same conclusion was arrived at by Grundlach (*Naturgeschichte der Honigbienen*, Cassel, 1842), and others; and that this is really the case, has been lately proved by a series of experiments undertaken expressly in reference to this question by Dumas and Milne Edwards, (*Ann. Ch. et Ph.*, 3me Series, Août, 1845, xiv. 400,) so that as respects the origin of wax, Dumas has given up his former opinions as untenable.

The composition of the varieties of wax seems to vary in the same way as that of the fat acids, and they appear, according to Löwig, to pass into each other by the addition of  $C_2 H_2$ : he gives the following formulæ in illustration of these transitions. (*Chem. d. Org. Verbind.*, ii. 213.)

|                            |                       |
|----------------------------|-----------------------|
| Bees' wax .....            | $C_{34} H_{34} O_2$   |
| Chinese wax .....          | } $C_{36} H_{36} O_2$ |
| Palm wax .....             |                       |
| Oxidized Chinese wax ..... | $C_{36} H_{36} O_3$   |
| Myrtle wax .....           | $C_{36} H_{36} O_5$   |
| Cerosine .....             | $C_{48} H_{48} O_2$   |
| Cerosinic acid.....        | $C_{48} H_{48} O_3$   |

It is remarkable that in all the varieties of wax (with the exception of that of the cork-tree) the atomic relation of the carbon to the hydrogen is 1 : 1.

i. *Bees' wax*, in its ordinary state, is yellow, and has a peculiar odor; it is usually bleached by exposing it in thin ribands upon the bleaching-ground, to the joint action of air, light, and moisture. Attempts have been made to whiten it by the agency of chlorine, but wax so bleached never burns well, a portion of chlorine always being retained. According to Ingenohl, (*Chem. Gaz.*, Sept. 1844,) wax may be expeditiously bleached as follows:—To a pound of melted wax add 2 ounces of pulverised nitrate of soda, and then, by degrees, 1 ounce of sulphuric acid previously diluted with 9 ounces of water, the whole being kept warm, and stirred; the vessel must be large, as the mixture rises considerably; when all the acid is added, it is allowed to cool somewhat, and the vessel filled with boiling water and set aside; the wax cake,

when cold, is removed, and conveyed into boiling water, so as to wash out all traces of sulphate of soda and of acid: it is then white, and should be perfectly free from nitric acid, which, if present, would render it liable to become yellow.

Pure wax is white, translucent, inodorous, tasteless, and insoluble in water; its sp. gr. is 0·960 to 0·966; it fuses at about 150°; at about 85° it admits of being kneaded and moulded. The sp. gr. of melted wax is 0·834 at 178°, and 0·8247 at 200° (water at 60° being = 1.) At and below 32° it is brittle and hard. It is almost entirely soluble in boiling alcohol, and in boiling ether; a small portion only is retained by the alcohol, when cold, and none by the ether.

When white bees' wax is subjected to dry distillation, margaric acid first passes over, then paraffine, and afterwards certain liquid hydrocarbons, olefiant gas and carbonic acid being at the same time evolved. The distilled product concretes into a buttery mass, and contains no sebacic acid. (GERHARDT. ETTLING. *Ann. der Pharm.*, ii. 253.) Distilled with lime, wax yields paraffine, carbonic acid, and water. (BUSSY.) When wax mixed with lime and caustic potassa is heated to about 440°, hydrogen is evolved and stearate of potassa formed. (LEWY, *Comptes rendus*, 1843, p. 675.) On melting wax and then dropping fused caustic potassa into it, a small quantity of gas is given off, and the whole mass becomes a gelatinous yellow soapy substance, almost entirely soluble in a large quantity of water. When this soap is decomposed by an acid an oily liquid separates, which concretes on cooling into a brittle substance soluble in hot alcohol, and separating in a crystalline state as the solution cools. Its fusing-point is 165°, and on concreting it exhibits no crystalline texture, nor has it any of the characters of stearic acid. It appears to be identical with the *Ceraine* of Ettling. (WARINGTON and FRANCIS, *Mem. Chem. Soc.*, i. 248.) When wax is digested at a moderate heat, with nitric acid, there is at first violent action, which gradually subsides, and after some days the wax is converted into an oily mass, which ultimately dissolves in the acid. On continuing the digestion till red fumes are no longer evolved, crystals of *Succinic acid* are obtained, and a rancid volatile oil evaporates. (GERHARDT. RONALDS. *Ann. der Pharm.*, xliii. 356.) When wax is boiled in a strong solution of caustic potassa, a difficultly soluble soap is formed, which separates upon the surface, and indurates on cooling; when this soap is decomposed by acids, the wax separates nearly unaltered in its properties. (CHEVREUL.)

The ultimate composition of wax has been determined by Gay Lussac and Thenard, Hess, and Lewy, with the following results:

|                | Gay Lussac<br>and Thenard. |      | Hess.  |      | Lewy<br>(bleached). |      | Lewy<br>(unbleached). |
|----------------|----------------------------|------|--------|------|---------------------|------|-----------------------|
| Carbon .....   | 81·79                      | .... | 81·52  | .... | 79·25               | .... | 80·20                 |
| Hydrogen ..... | 12·67                      | .... | 13·23  | .... | 13·24               | .... | 13·44                 |
| Oxygen .....   | 5·54                       | .... | 5·25   | .... | 7·51                | .... | 6·36                  |
| <hr/>          |                            |      |        |      |                     |      |                       |
| Wax .....      | 100·00                     |      | 100·00 |      | 100·00              |      | 100·00                |

Löwig assigns to wax the formula C<sub>34</sub> H<sub>34</sub> O<sub>2</sub>, which would give

|                |    |      |     |      |        |
|----------------|----|------|-----|------|--------|
| Carbon.....    | 34 | .... | 204 | .... | 80·31  |
| Hydrogen ..... | 34 | .... | 34  | .... | 13·38  |
| Oxygen .....   | 2  | .... | 16  | .... | 6·31   |
| <hr/>          |    |      |     |      |        |
| Wax .....      | 1  |      | 254 |      | 100·00 |



When wax is boiled in alcohol about nine-tenths is dissolved, but falls again on cooling; to this soluble portion John gave the name of *Cerine*, and termed the insoluble portion *myricine*. Boudet and Boissenot, (*Journ. de Pharm.*, xiii. 43,) and Ettling, concur in this statement, but regard cerine and myricine as isomeric bodies. Hess (*Ann. der Pharm.*, xxvii. 8), and Van der Vliet (*Bulletin de Néerlande*, 1838,) regard wax as a simple substance  $=C_{20}H_{20}O$ , susceptible of oxidization; in yellow wax this substance is combined with a coloring matter, and in white wax with *cerainic acid*. Upon the whole it would appear that wax is of variable composition, and that myricine is sometimes absent. (LÖWIG.)

ii. *Myrtle wax*. The berries of several species of *Myrica*, especially the *Myrica cerifera*, which flourishes in Louisiana, yield a considerable quantity of a hard brittle wax; it forms an incrustation upon the berries, and is separated by boiling them in water; it is of a pale-green color; sp. gr. 1.015; it fuses at about  $110^{\circ}$ . Boiling alcohol dissolves about one-twentieth of its weight, but lets most of it fall on cooling; hot ether dissolves about one-fourth of its weight, and deposits it on cooling in crystalline plates like spermaceti, the ether acquiring a green color; it is sparingly soluble in oil of turpentine, and alkalis act upon it as on bees' wax. (BOSTOCK, *Nicholson's Journ.*, iv. 130.) The wax of the *Myrica cordifolia*, a shrub which grows at the Cape of Good Hope, appears to resemble the preceding. (JOHN, *Chem. Untersuchungen*, iii. 38.) According to Chevreul, myrtle wax is a margarate and oleate of glycerine. Its ultimate analysis gives the following results:

|                 |    |     |     |     |        | Lewy.  |
|-----------------|----|-----|-----|-----|--------|--------|
| Carbon .....    | 36 | ... | 216 | ... | 74.00  | 74.23  |
| Hydrogen .....  | 36 | ... | 36  | ... | 12.32  | 12.07  |
| Oxygen .....    | 5  | ... | 40  | ... | 13.68  | 13.70  |
| <hr/>           |    |     |     |     |        |        |
| Myrtle wax .... | 1  |     | 292 |     | 100.00 | 100.00 |

iii. *Palm wax*. *Carnauba wax*. *Brazilian wax*. These names have been applied to a hard brittle wax coming from Rio Janeiro, and resembling that described by Humboldt as the produce of the *Ceroxylon Andicola*. (BRANDE, *Phil. Trans.*, 1811.) It forms a secretion upon the stems and leaves of the palms. It dissolves in boiling alcohol and ether, but the greater part separates as the solutions cool, and in some cases a little resin is retained by the alcohol. The fusing-point of palm wax is about  $160^{\circ}$ ; that of carnauba wax  $180^{\circ}$ , and of some of the varieties of Brazilian wax,  $206^{\circ}$ . Analyzed by Boussingault and Lewy, these waxes yielded

|               |    |     |     |     |        | Palm wax. |               | Carnauba wax. |  |
|---------------|----|-----|-----|-----|--------|-----------|---------------|---------------|--|
|               |    |     |     |     |        | Lewy.     | Boussingault. | Lewy.         |  |
| Carbon .....  | 36 | ... | 216 | ... | 80.59  | 80.48     | 81.6          | 80.36         |  |
| Hydrogen .... | 36 | ... | 36  | ... | 13.42  | 13.29     | 13.3          | 13.07         |  |
| Oxygen .....  | 2  | ... | 16  | ... | 5.99   | 6.23      | 5.1           | 6.57          |  |
| <hr/>         |    |     |     |     |        | <hr/>     |               | <hr/>         |  |
| Palm wax .... | 1  |     | 268 |     | 100.00 | 100.00    | 100.0         | 100.00        |  |

iv. *Chinese wax*. *Japan wax*. This substance is the produce of the *Rhus succedaneum*. It is white and crystalline, resembling spermaceti; it fuses at about  $180^{\circ}$ . It is very sparingly soluble in alcohol and in

boiling ether, but readily soluble in naphtha. It forms a soluble soap when boiled in a solution of caustic potassa. It contains no glycerine. Its formula, according to Lewy, is the same as that of palm and carnauba wax, namely,  $C_{36}H_{36}O_2$ .

v. *Ocuba wax* is the produce of the *Myristica Ocuba*, a shrub growing in the province of Pera. It is yellow, soluble in boiling alcohol, and its fusing-point is  $196^{\circ}$ . In composition it resembles myrtle wax, being  $C_{36}H_{36}O_5$ . (LEWY.)

vi. *Sugar-cane wax. Cerosine.* This is the waxy substance which is found upon the sugar-cane, especially upon the blue variety, which is comparatively hard and ligneous, and yields but little juice. (AVEQUIN. *Ann. Ch. et Ph.*, LXXV. 219.) It fuses at  $180^{\circ}$ , and forms a crystalline mass on cooling; it is insoluble in cold, but soluble in boiling alcohol, and the alcoholic solution, even when containing but a small quantity of the wax, congeals on cooling into a gelatinous mass, resembling the alcoholic solution of soap; it is insoluble in cold, and very sparingly soluble in boiling ether. It is difficultly saponifiable. It has been analyzed by Dumas, (*Ann. Ch. et Ph.*, LXXV. 222,) and by Lewy; it consists of

|                |    |     |     |     |        | Dumas. |       | Lewy. |        |
|----------------|----|-----|-----|-----|--------|--------|-------|-------|--------|
| Carbon .....   | 48 | ... | 288 | ... | 81·82  | ...    | 81·4  | ...   | 81·74  |
| Hydrogen ..... | 48 | ... | 48  | ... | 13·63  | ...    | 14·0  | ...   | 13·64  |
| Oxygen .....   | 2  | ... | 16  | ... | 4·55   | ...    | 4·6   | ...   | 4·62   |
| <hr/>          |    |     |     |     |        |        |       |       |        |
| Cerosine ..... | 1  |     | 352 |     | 100·00 |        | 100·0 |       | 100·00 |

When cerosine is intimately mixed with potassa and lime, and heated to  $480^{\circ}$ , pure hydrogen is evolved, and a white mass remains, from which, when boiled in dilute hydrochloric acid, *cerosinic acid* separates; when purified this acid consists, according to Lewy, of  $C_{48}H_{48}O_3$ .

vii. *Cork-tree wax.* This substance is obtained by boiling the bark of the *Quercus suber*, or *cork*, in alcohol; when the alcohol is distilled off, the cork wax crystallizes in yellow crystals, which may be purified by repeated solution and crystallization. (CHEVREUL, *Ann. de Chim.*, xvi. 170.) It forms yellow acicular crystals, which soften and sink in boiling water. This substance, when heated in a glass tube, decomposes before fusion; upon platinum foil it burns with a bright flame and diffuses a peculiar odor. It is not acted on by boiling solution of potassa. Nitric acid converts it into a peculiar acid (*cerinic acid*)  $=C_{14}H_{11}O_4$ . (DÖPPING, *Ann. der Pharm.*, XLV. 289.) Sulphuric acid blackens and dissolves it. The components of this species of wax are

|                |    |     |     |     |        | Döpping. |        |
|----------------|----|-----|-----|-----|--------|----------|--------|
| Carbon .....   | 22 | ... | 132 | ... | 75.85  | ...      | 75.63  |
| Hydrogen ..... | 18 | ... | 18  | ... | 10.38  | ...      | 10.55  |
| Oxygen .....   | 3  | ... | 24  | ... | 13.77  | ...      | 13.82  |
| <hr/>          |    |     |     |     |        |          |        |
| Cork wax ..... | 1  |     | 174 |     | 100.00 |          | 100.00 |

PROXIMATE COMPONENTS OF FATS AND OILS. GLYCERINE. FAT-ACIDS. It has been above stated, that the oils and fats both of vegetable and animal origin are natural combinations of, or at least that they are resolvable into, a peculiar base, termed *glycerine*, or *oxide of glyceryle*, and certain fatty acids; that in fact they may be represented as *salts of glyce-*



rine; and that in the process of saponification these salts are decomposed by the more powerful alkaline bases, *soaps being compounds of the alkalis with the fatty acids*, in the formation of which the glycerine is set free\*. In the preceding details certain of these fatty acids have been adverted to; it remains here to notice those which are of most frequent occurrence in the common fats and oils, namely, the stearic, margaric, and oleic acids, and to describe the sources, properties, and composition of glycerine.

GLYCERINE.  $C_6H_7O_5, HO$  (*γλυκὺς*, *sweet*.) This substance, under the name of the *sweet principle of oils*, was discovered by Scheele (*Opuscula*, ii. 175,) and more fully examined by Chevreul (*Recherches sur les Corps Gras*, 209, 238.) It is obtained by boiling a mixture of finely-pulverized oxide of lead, or, which is better, freshly precipitated hydrated oxide of lead, with any of the common fats or oils, and water; the water should be poured off and renewed from time to time during the process, and ultimately, the aqueous solution of glycerine thus obtained is freed from lead by a current of sulphuretted hydrogen, filtered, carefully evaporated to the consistency of syrup, and then exposed in vacuo over oil of vitriol, till it no longer loses weight.

\* The common *hard soaps* of this country are chiefly made with tallow and soda, they are therefore stearates, margarates, and oleates of soda. The sp. gr. of the solution of caustic soda is about 1050, and is prepared in the usual way by the action of quicklime upon carbonate of soda. When the ley is raised to its boiling-point, the tallow is gradually added as long as the ley saponifies it, and in this way a liquor is obtained, which holds the soap and glycerine in solution; to separate the former, common salt is added; soap being insoluble in brine, is thus brought to float upon the surface, and if the brine be concentrated, the soap separates nearly in an anhydrous state, but as this is not the object of the manufacturer, the quantity of salt employed is only such as to effect the separation of the soap, without dehydrating it. New soap is said to contain about 50 *per cent.* of water, and to retain above 30 *per cent.* when comparatively hard and dry. There is therefore a manifest advantage to the consumer in purchasing dry and old soap, while the object of the vender is to sell the soap as humid as possible, and to prevent its desiccation, which is effected by keeping it in damp cellars, or in an atmosphere saturated with aqueous vapor. Soap is sometimes colored, mottled, or marbled, by the addition of coloring matters when in its pasty state; sometimes a solution of sulphate of iron is used for this purpose, which being decomposed, causes the diffusion of oxide of iron through the soap; in these cases the mottling is originally black, but becomes brown upon the exterior of the bars in consequence of the

action of the air. A considerable quantity of common rosin is added to the yellow soaps of commerce. There are also other additions made to soap, some of which are supposed to improve its detergent quality, but generally speaking, they rather deteriorate the article than otherwise, and are principally resorted to as adding to the weight of the soap by the substitution of cheap materials; sand, clay, fuller's earth, finely pulverised flints, Cornish clay, starch, flour, and many other things, have been thus employed.

The soaps known in commerce as *Spanish soap* and *Marseilles soap*, are soda soaps of olive-oil. Palm-oil and cocoa-nut oil, are also largely used as sources of soap, and mixtures of these with the animal fats are employed as the basis of scented and other toilet soaps.

The soaps of potassa are distinguished from those of soda by remaining *soft*; common soft soap is frequently made with fish oil. *Naples soap* is a perfumed potassa soap made with lard. *Transparent soap* is obtained by dissolving soap in alcohol, which is afterwards distilled off, so as to leave a soft transparent residue, which is dried in moulds or balls. (In reference to the varieties of soap, and the details of the manufacture, see DUMAS, *Chim. App. aux Arts*, vi. 706, and URE'S *Dictionary of Arts and Manufactures*.)

When the fats and oils are decomposed by oxide of lead, the resulting combination of the fatty acids with that oxide, is known under the name of *plaster*. (*Emplastrum plumbi. Diachylon*.)

Glycerine is also abundantly produced in the process of the saponification of fat and oil by potassa or soda; after the separation of the soap the liquor should be rendered neutral by the addition of dilute sulphuric acid, filtered, and evaporated to a syrupy consistence; from this residue the glycerine may be extracted by alcohol and evaporation.

Glycerine, when pure, is a thick uncrystallizable syrup, sp. gr. 1.28; it is sweet, inodorous, soluble in all proportions in water and in alcohol, but insoluble in ether. It acts, notwithstanding its viscosity, much in the same way as water, as a solvent of salts. It dissolves baryta, strontia, and oxide of lead, but the other metallic oxides which are insoluble in water, are also insoluble in glycerine. It occasions no precipitate in solution of subacetate of lead. When heated in a retort, glycerine partly distils over unchanged, and is partly decomposed, yielding the characteristic vapor of *acroleine* (p. 1250.) It is not susceptible of fermentation. (PELOUZE, *Ann. Ch. et Ph.*, LXiii. 20.) According to Redtenbacher, however, when left for some months in a warm place, mixed with a little yeast, it undergoes a slow fermentation, producing metacetic and formic acids. (*Ann. der Pharm.*, LViii. 174.) It is decomposed by nitric acid with the formation of oxalic acid, carbonic acid, and water. Mixed with peroxide of manganese and hydrochloric acid, or dilute sulphuric acid, it is rapidly decomposed, and yields carbonic and formic acids. When mixed with twice its weight of sulphuric acid, it is not blackened, but there is considerable elevation of temperature. After the mixture has cooled, if it be diluted, saturated with milk of lime, and filtered, it yields on evaporation a syrupy liquor, from which crystals of a peculiar salt of lime are deposited: they contain a peculiar acid, the *sulphoglyceric*.

By acting upon glycerine by a mixture of 2 volumes of sulphuric and 1 of nitric acid, and then adding water, Sobrero obtained a yellowish oil-like compound, inodorous, but of a sweet and pungent taste, and inducing head-ache when merely applied to the tongue. (*Comptes rendus*, &c., February, 1847.) When left for some months in contact of chlorine, glycerine gradually gives rise to the formation of hydrochloric acid, and a viscid liquid =  $C_{12}H_{11}O_{10}, Cl_3$ . A similar compound is formed with bromine. Iodine dissolves in glycerine, but is without further action. (PELOUZE.) The elements of *hydrated glycerine* may be represented as

|                           |   |     |    |     |        |     |          |
|---------------------------|---|-----|----|-----|--------|-----|----------|
|                           |   |     |    |     |        |     | Pelouze. |
| Carbon .....              | 6 | ... | 36 | ... | 39·13  | ... | 39·44    |
| Hydrogen .....            | 8 | ... | 8  | ... | 8·69   | ... | 8·73     |
| Oxygen .....              | 6 | ... | 48 | ... | 52·18  | ... | 51·83    |
| <hr/>                     |   |     |    |     |        |     |          |
| Hydrate of glycerine .... | 1 |     | 92 |     | 100·00 |     | 100·00   |

In combination with the fatty acids, and as an element of the sulphoglyceric acid, the glycerine is presumed to be *anhydrous*; in those states of combination its equivalent is 83, and its elements

|                          |   |     |    |     |        |
|--------------------------|---|-----|----|-----|--------|
| Carbon .....             | 6 | ... | 36 | ... | 43.37  |
| Hydrogen .....           | 7 | ... | 7  | ... | 8.43   |
| Oxygen .....             | 5 | ... | 40 | ... | 48.20  |
| <hr/>                    |   |     |    |     |        |
| Anhydrous glycerine..... | 1 |     | 83 |     | 100.00 |



It is assumed that glycerine is the oxide of a hydrocarbon (*glyceryle*)  $= C_6 H_7$ ; but it is contrary to analogy that an oxide, containing 5 atoms of oxygen, should be *basic*. Stenhouse (*Ann. der Pharm.*, xxxvi. 25,) has inferred that the atomic constitution of glycerine, as it exists in combination with the fatty acids, is  $C_3 H_2 O$ ; and that when these compounds are decomposed, 2 equivalents of the glycerine so constituted, combine with 3 of water to form ordinary hydrated glycerine. Some later experiments, too, of Pelouze, quoted by Löwig, indicate the formula for hydrated glycerine dried at  $250^\circ$  to  $260^\circ$  as  $= C_6 H_8 O_2$ . The assumption, however, that glycerine is an oxide of glyceryle, and that the fats and oils are proximately constituted of glycerine combined with the fatty acids, after the manner of saline combinations, is altogether hypothetical. Berzelius regards the fats as peculiar organic products, which agree in their susceptibility of being resolved by alkalis and other salifiable bases, into fatty acids and glycerine, partly under catalytic influences, and partly as the results of affinity.

STEARIC ACID.  $C_{68} H_{66} O_5 + 2 HO = \overline{St}, 2HO$ . Stearine, which is a component of all the harder and less fusible fats, and which exists in them in increasing proportions as their points of fusion approach  $142^\circ$ , is regarded as a compound of stearic acid and glycerine. In its ordinary state stearic acid is a *hydrate*, and *anhydrous stearic acid* has not been isolated, but its composition, as inferred from the analysis of certain of its compounds, is

|                             |    |      |     |      |        |
|-----------------------------|----|------|-----|------|--------|
| Carbon .....                | 68 | .... | 408 | .... | 79.37  |
| Hydrogen .....              | 66 | .... | 66  | .... | 12.84  |
| Oxygen .....                | 5  | .... | 40  | .... | 7.79   |
| <hr/>                       |    |      |     |      |        |
| Anhydrous stearic acid..... | 1  |      | 514 |      | 100.00 |

*Hydrated stearic acid* may be obtained from mutton suet or tallow, 4 parts of which are boiled with 4 parts of water and 1 part of caustic potassa; the resulting soap is then dissolved in 6 parts of warm water, and to this solution 45 parts of cold water are subsequently added, and the mixture left at a temperature of  $60^\circ$ , when it gradually deposits flakes of *bistearate of potassa*, mixed with a little margarate and oleate of potassa. The supernatant liquor is then carefully saturated by an acid, and diluted with water, when a second portion of the bistearate falls. It is collected, dried, and dissolved in 20 to 24 parts of boiling alcohol; as this solution cools, the bistearate falls down, free from oleate, and nearly free from margarate of potassa. In order to free it entirely from margaric acid, it must be repeatedly re-dissolved in boiling alcohol, and allowed to deposit as before. When thus purified, it is decomposed by boiling it in dilute hydrochloric acid; the stearic acid thus separated is well washed with hot water, and dissolved in boiling alcohol, which, on cooling, deposits it in white crystalline flakes, which fuse at about  $165^\circ$ , are perfectly insoluble in water, readily soluble in all proportions in boiling alcohol, and soluble in boiling ether. The hot solution of equal parts of stearic acid and alcohol solidifies on cooling. The alcoholic solution reddens litmus. Stearic acid burns with a white

flame resembling wax\*. In its solid state its specific gravity is 1·01; but in a fused state, only 0·854 (CHEVREUL.) The formula of the acid in this state is  $C_{68}H_{66}O_5, 2HO$ , its elements being

|                           |    |      |     |      |        | Varrentrapp. | Stenhouse. |
|---------------------------|----|------|-----|------|--------|--------------|------------|
| Carbon .....              | 68 | .... | 408 | .... | 76·69  | .... 76·53   | .... 76·8  |
| Hydrogen .....            | 68 | .... | 68  | .... | 12·76  | .... 12·95   | .... 12·8  |
| Oxygen .....              | 7  | .... | 56  | .... | 10·55  | .... 10·52   | .... 10·4  |
| <hr/>                     |    |      |     |      |        |              |            |
| Hydrated stearic acid.... | 1  |      | 532 |      | 100·00 | 100·00       | 100·0      |

When stearic acid is subjected to distillation, it yields margaric acid and margarone, carburetted hydrogen and carbonic acid gas, and water. Stearic acid is also converted into margaric acid by sulphuric, and by chromic acid. Heated with nitric acid, a violent action ensues, after a time nitric oxide is evolved, and the margaric acid, which is the first result of the action, is ultimately converted into succinic and suberic acids. Pimelic, adipic, lipic, and œnanthylic acids are also formed. (REDTENBACHER, *Ann. der Pharm.*, xxxv. 46.) Fused with anhydrous phosphoric acid, stearic acid yields a substance which is nearly insoluble in alcohol, and fusible at about  $135^{\circ}$  into a yellow liquid, which concretes on cooling into a brittle friable mass, no longer acid, and being, according to Erdmann,  $C_{68}H_{65}O_4$ .

When stearic acid, mixed with one-fourth its weight of quicklime, is subjected to dry distillation, a substance passes over fusible at about  $185^{\circ}$ , and sparingly soluble in alcohol and ether. It has been termed *stearone*. (BUSSY, *Journ. de Pharm.*, xix. 643, and *Ann. Ch. et Ph.*, Liii. 410.) Its formula appears to be  $C_{68}H_{62}O$ .

The *salts of the stearic acid* have been chiefly examined by Chevreul. The neutral stearates of the alkalis are soluble in water, and when acted on by a large quantity of water, are partially resolved into acid stearates.

Stearic acid is *bibasic*, so that in what may be termed the neutral stearates, 1 atom of acid is combined with 2 atoms of base; but there are also salts in which 1 atom of fixed base may be replaced by 1 atom of water; the anhydrous stearic acid is represented by the symbol  $\overline{St}$ .

*Stearate of Ammonia.*  $2NH_4O, \overline{St}$ . Hydrated stearic acid absorbs gaseous ammonia, and a white and almost inodorous compound is formed: it may be sublimed in vacuo, with the loss of some ammonia. It is soluble in a dilute hot aqueous solution of ammonia, and on cooling deposits nacreous scales, which are probably  $NH_4O, HO, \overline{St}$ .

*Stearate of Potassa.*  $2KO, \overline{St}$ . When equal weights of stearic acid

\* In the manufacture of *stearic candles*, the substance principally employed is the stearic acid of tallow, to obtain which, the tallow is saponified by lime, and the resulting stearate and oleate of lime is decomposed by means of dilute sulphuric acid. The stearic and oleic acids thus obtained are separated by pressure, the oleic acid being used in the manufacture of soap. The crystalline texture of the stearic acid, which would render the candle inconve-

niently brittle, is modified or destroyed by the addition of a very small quantity of magnesia, or of finely-pulverised French chalk, or steatite; white arsenic was originally used for this purpose, and is still sometimes employed; it is of course highly dangerous and deleterious; it is fortunately easily recognized by the garlic odor which the glowing wick of the candle exhales, after the flame has been blown out.



and hydrate of potassa are boiled together in 20 parts of water, an opaque granular deposit of the above stearate is formed as the liquor cools. It may be purified by solution in hot alcohol, when it forms shining scales of a greasy feel, and weak alkaline taste. This salt is permanent in the air, and does not fuse when heated. It is entirely soluble in 25 parts of boiling water, but when dissolved in 100 parts of boiling water, a portion of acid stearate is deposited as the liquor cools. This acid stearate is best obtained by the action of a large quantity of cold water upon the neutral salt, and when deposited from its alcoholic solution, it forms delicate lamellar crystals, which soften but do not fuse at  $212^{\circ}$ .

*Stearate of Soda.*  $2\text{NaO}, \overline{\text{St}}$ , is formed by boiling 20 parts of stearic acid with 13 of hydrate of soda in 300 of water: the resulting compound is then dissolved in boiling alcohol, and is deposited as the solution cools, either in lamellar crystals, or as a hard translucent soap, sparingly soluble in cold water; it dissolves in about 20 parts of boiling water, and when this solution is mixed with 2000 parts of cold water, an *acid stearate* is deposited  $=\text{NaO}, \text{HO}, \overline{\text{St}}$ .

*Stearate of Baryta.*  $2\text{BaO}, \overline{\text{St}}$ , is a white, insipid, fusible powder, insoluble in boiling water and in boiling alcohol.

*Stearate of Lime and Stearate of Strontia* resemble the barytic salt.

*Stearate of Lead*,  $2\text{PbO}, \overline{\text{St}}$ , is thrown down in the form of a white fusible insoluble powder, when nitrate of lead is added to a boiling solution of neutral stearate of potassa. *Acid stearate of lead*,  $=\text{PbO}, \text{HO}, \overline{\text{St}}$ , is formed by fusing together 21 parts of oxide of lead and 100 of stearic acid: it is a grey radiated compound, fusible at  $212^{\circ}$ , and soluble in 60 parts of boiling alcohol (sp. gr. 0.823). *Basic stearate of lead*  $= 4\text{PbO}, \overline{\text{St}}$ , is formed by boiling stearic acid out of contact of air, in a solution of subacetate of lead; it is a hard transparent compound, fusible at  $212^{\circ}$ .

STEARINE. *Stearate of Glycerine.* When tallow or purified mutton suet is triturated with cold ether till it no longer loses weight, the residue is *stearine*. If the suet be fused in a water-bath, and then agitated with 5 or 6 times its volume of ether, it also leaves pure stearine. (LECANU.) When stearine has been subjected to pressure, it resembles stearic acid in appearance. After fusion it concretes into a translucent, brittle, and friable crystalline mass, fusible at about  $145^{\circ}$ . It is insoluble in water, and in cold alcohol, and therefore deposited from its solution in boiling alcohol. Boiling ether dissolves it in considerable quantity, but the greater part separates as the solution cools. Subjected to dry distillation, stearine yields margarine, margaric acid, and acroleine. The decomposition of stearine by the more powerful basic oxides has been already described.

The following are the ultimate elements of stearine:

|               |    |      |     |      |        | Pelouze. |        | Liebig. |        | Beetz. |        |
|---------------|----|------|-----|------|--------|----------|--------|---------|--------|--------|--------|
| Carbon .....  | 71 | .... | 426 | .... | 77·31  | ....     | 76·14  | ....    | 76·60  | ....   | 76·25  |
| Hydrogen....  | 69 | .... | 69  | .... | 12·51  | ....     | 12·30  | ....    | 12·29  | ....   | 12·45  |
| Oxygen.....   | 7  |      | 56  | .... | 10·18  | ....     | 11·56  | ....    | 11·11  | ....   | 11·30  |
| <hr/>         |    |      |     |      |        |          |        |         |        |        |        |
| Stearine .... | 1  |      | 551 |      | 100·00 |          | 100·00 |         | 100·00 |        | 100 00 |

These numbers are not consistent with the theoretical composition of

stearine, which represents it as a stearate of glycerine; it may, however, be doubted how far they are perfectly correct; and it will moreover appear in reference to what has been stated respecting its ultimate composition and atomic equivalent, that there are also discrepancies respecting glycerine.

**MARGARIC ACID.**  $C_{34}H_{33}O_3 + HO = \overline{Mg}, HO$ . The substance usually resorted to as a source of margaric acid is olive oil; it is saponified by potassa, and the aqueous solution of the resulting soap is decomposed by acetate of lead, which forms a precipitate composed of oleate and margarate of lead; this is dried and repeatedly boiled in ether, which dissolves the oleate and leaves margarate of lead; this is then decomposed by an acid, and the margaric acid which separates is purified by solution in alcohol and crystallization. Margaric acid may also be obtained by boiling pure stearic acid with its weight of nitric acid, for about 15 minutes; on cooling, the margaric acid concretes on the surface, and may be purified by pressing it between paper and crystallization from its alcoholic solution. This acid may also be obtained from butter. (See *Milk*.)

Margaric acid is a white, inodorous, tasteless, crystalline substance; when pure, its point of fusion, or rather of congelation, is  $140^{\circ}$ ; if above that point it contains stearic acid, if below, oleic acid. It is insoluble in water, but readily soluble in boiling alcohol and ether, and these solutions redden litmus. It falls in pearly scales as its alcoholic solution cools.

*Anhydrous margaric acid* has not been isolated: its ultimate composition is represented as

|                              |    |     |     |     |        | Chevreul. |
|------------------------------|----|-----|-----|-----|--------|-----------|
| Carbon.....                  | 34 | ... | 204 | ... | 78·16  | .... 79·1 |
| Hydrogen .....               | 33 | ... | 33  | ... | 12·64  | .... 12·0 |
| Oxygen .....                 | 3  | ... | 24  | ... | 9·20   | .... 8·9  |
| <hr/>                        |    |     |     |     |        |           |
| Anhydrous margaric acid .... | 1  |     | 261 |     | 100·00 | 100·0     |

The *crystallized margaric acid* has been repeatedly analyzed; its components are

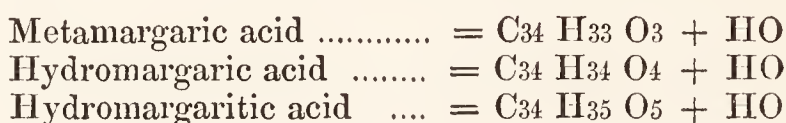
|                             |    |     |     |     | Varrentrapp. | Bromeis. | Erdmann. |     |        |
|-----------------------------|----|-----|-----|-----|--------------|----------|----------|-----|--------|
| Carbon .....                | 34 | ... | 204 | ... | 75.55        | ...      | 75.66    | ... | 75.55  |
| Hydrogen .....              | 34 | ... | 34  | ... | 12.59        | ...      | 12.69    | ... | 12.55  |
| Oxygen .....                | 4  | ... | 32  | ... | 11.86        | ...      | 11.65    | ... | 11.90  |
| <hr/>                       |    |     |     |     |              |          |          |     |        |
| Hydrated margaric acid .... | 1  |     | 270 |     | 100.00       |          | 100.00   |     | 100.00 |

These numbers represent margaric acid as monobasic; Erdmann regards as a bibasic acid  $= C_{68}H_{66}O_6 + 2HO$ . (LÖWIG, *Chem. d. Org. verbind*, II. 181.)

When margaric acid is heated in a retort, the greater part passes over unchanged, but there is also a little carbonic acid and margarone formed. Distilled with one-fourth its weight of quicklime, margaric acid yields a considerable quantity of *margarone* ( $= C_{34}H_{33}O$ ), together with a liquid compound of similar composition. (BUSSY, *Ann. Ch. et Ph.*, liii. 398.) Margarone, when purified by crystallization from alcohol, is a white solid of a pearly lustre, fusible at  $170^{\circ}$ , volatile without decomposition, and not altered by boiling with solution of potassa.



When margaric acid is boiled for some days with nitric acid, it is resolved into suberic and succinic acids and water. (BROMEIS.) By the action of sulphuric acid on olive oil, Fremy (*Comptes Rendus*, 1837, No. 22; *Ann. der Pharm.*, xx. 50,) obtained a *sulphomargaric acid* and *sulpholeic acid*, together with other apparently peculiar fat acids, namely:



*Salts of the Margaric acid.* Margaric acid forms neutral, acid, and basic salts; of these, the neutral salts of the alkalis are soluble in water, but when there is great excess of water they lose a part of their base, and become acid salts. When margaric acid is triturated with a cold solution of carbonate of potassa, margarate and bicarbonate of potassa are produced, but at  $212^\circ$  margarate of potassa is formed and carbonic acid expelled.

*Margarate of Ammonia.* When hydrated margaric acid is saturated by exposure to gaseous ammonia, or digested in dilute aqueous ammonia, small crystalline scales of a pearly lustre are obtained,  $=\text{NH}_4 \text{O}, 2\overline{\text{Mg}}$ . They dissolve in a strong aqueous solution of ammonia, forming a gelatinous combination.

By passing ammoniacal gas into olive oil so as to saponify it, and then allowing the excess of ammonia to escape by exposure to air at a temperature between  $80^\circ$  and  $90^\circ$ , and treating the residue with boiling water, and purifying the resulting product by solution and crystallization from boiling alcohol, Boullay obtained a white neutral substance, which he terms *margaramide*  $= \text{NH}_2 + \text{C}_{34} \text{H}_{33} \text{O}_2$ : it appears to be formed in consequence of the union of 1 atom of the oxygen of the margaric acid with 1 atom of the hydrogen of the ammonia. It fuses at  $140^\circ$ , is insoluble in water, but soluble in hot alcohol and ether, and burns with a smoky flame. Boiled in a strong solution of potassa, it evolves ammonia and forms margarate of potassa. Its ultimate elements are

|                   |    |      |     |      |       | Boullay.   |
|-------------------|----|------|-----|------|-------|------------|
| Carbon.....       | 34 | .... | 204 | .... | 75.8  | .... 75.68 |
| Hydrogen .....    | 35 | .... | 35  | .... | 13.0  | .... 13.08 |
| Oxygen .....      | 2  | .... | 16  | .... | 6.0   | .... 5.91  |
| Nitrogen .....    | 1  | .... | 14  | .... | 5.2   | .... 5.33  |
| <hr/>             |    |      |     |      |       | <hr/>      |
| Margaramide ..... | 1  |      | 269 |      | 100.0 | 100.00     |

*Margarate of Potassa*,  $\text{KO}, \overline{\text{Mg}}$ , is formed by boiling equal parts of margaric acid and hydrate of potassa in 5 parts of water, washing the salt which separates with a little water, drying it by pressure, and dissolving it in boiling alcohol; on cooling, the salt is obtained in brilliant scales; 1 part dissolved in 10 of cold water, forms a turbid solution which becomes clear at  $160^\circ$ . A solution of 1 part of margarate of potassa in 6 of boiling alcohol concretes on cooling; a solution of this salt in 20 parts of boiling water, when mixed with 1000 parts of cold water, deposits *bimargarate of potassa*, and by the further action of cold water, further portions of alkali may be abstracted, leaving salts with proportionate excess of acid.

*Margarate of Soda*,  $\text{Na O}, \overline{\text{Mg}}$ , when in concentrated aqueous solution is gelatinous when hot, and concretes on cooling: it is very soluble in alcohol, and is partially decomposed by the action of a large quantity of cold water, soda being abstracted, and an acid margarate remaining in the form of a pearly salt.

*Margarate of Baryta*,  $\text{Ba O}, \overline{\text{Mg}}$ , is precipitated in the form of a white powder on mixing a solution of chloride of barium with a solution of margarate of soda in dilute alcohol.

*Margarate of Lead*,  $\text{Pb O}, \overline{\text{Mg}}$ , may be obtained by the mutual decomposition of acetate of lead and margarate of soda. It falls in the form of a bulky white insoluble precipitate, fusible by heat. By digesting this neutral salt in a solution of subacetate of lead, it is gradually converted into a granular basic salt, consisting of 2 atoms of margarate, combined with 1 atom of sexbasic acetate of lead. (VARRENTRAPP, *Ann. der Pharm.*, xxxvi. 65.)

*Margarate of Silver*,  $\text{Ag O}, \overline{\text{Mg}}$ , forms a white voluminous precipitate, which slowly darkens in color on exposure to light. It has been analyzed with the following results:

|                       |    |      |     |      |        | Redtenbacher. | Bromeis.   |
|-----------------------|----|------|-----|------|--------|---------------|------------|
| Carbon .....          | 34 | .... | 204 | .... | 54.11  | .... 54.57    | .... 54.09 |
| Hydrogen .....        | 33 | .... | 33  | .... | 8.75   | .... 8.92     | .... 8.72  |
| Oxygen .....          | 3  | .... | 24  | .... | 6.53   | .... 6.56     | .... 6.20  |
| Oxide of silver ..... | 1  | .... | 116 | .... | 30.61  | .... 29.95    | .... 30.99 |
| <hr/>                 |    |      |     |      |        |               |            |
| Margarate of silver   | 1  |      | 377 |      | 100.00 | 100.00        | 100.00     |

MARGARINE. *Margarate of Glycerine*. It is probably impossible to obtain a perfectly pure margarine. When the fats which contain it are triturated and washed with ether, the ethereal solution leaves on evaporation a mixture of margarine and oleine, and if this residue be boiled in alcohol, it deposits margarine on cooling, and the oleine is retained by the alcohol. Olive oil, linseed oil, and butter, are probably the best sources of margarine, more especially the solid part of olive oil deposited on cooling it, and subjected to pressure so as to separate as much of the oleine as can in that way be squeezed out of it.

Margarine fuses at  $120^{\circ}$ . It dissolves in boiling alcohol and is deposited on cooling, similar to stearine. 1 part of margarine is retained in permanent solution by 10 parts of ether at the temperature of  $60^{\circ}$ , whereas stearine under the same circumstances is almost entirely deposited.

OLEIC ACID.  $\text{C}_{44}\text{H}_{40}\text{O}_4 + \text{HO} = \overline{\text{O}}, \text{HO}$ . This, like the preceding acids, has not been isolated in an anhydrous state. Its elements, as it exists in combination, are

|                           |    |      |     |      |        |
|---------------------------|----|------|-----|------|--------|
| Carbon .....              | 44 | .... | 264 | .... | 78.51  |
| Hydrogen .....            | 40 | .... | 40  | .... | 11.91  |
| Oxygen .....              | 4  | .... | 32  | .... | 9.58   |
| <hr/>                     |    |      |     |      |        |
| Anhydrous oleic acid .... | 1  |      | 336 |      | 100.00 |

*Hydrated oleic acid* is best obtained by saponifying almond oil or olive oil with potassa, and decomposing the soap by hydrochloric acid, which separates a mixture of oleic and margaric acids; this, by digestion



with oxide of lead, is converted into oleate and margarate of lead, and by digesting these oleates in ether, an acid oleate of lead is dissolved, leaving margarate and basic oleate of lead. The ethereal solution is mixed with its bulk of water and decomposed by the addition of a sufficient quantity of hydrochloric acid, which throws down chloride of lead and leaves the oleic acid in solution, from which it is obtained by careful evaporation. To obtain it perfectly pure, Varrentrapp recommends that it should be saponified with carbonate of soda, and the resulting soap dissolved in water, separated by the addition of common salt, and decomposed by tartaric acid, and that this operation should be repeated till the oleic acid is obtained perfectly free from color. The crude oleic acid which is abundantly produced in the manufacture of stearine candles, may be similarly purified. The elements of the acid thus obtained are

|                          |    |      |     |      |        | Varrentrapp. |        |
|--------------------------|----|------|-----|------|--------|--------------|--------|
| Carbon .....             | 44 | .... | 264 | .... | 76.52  | ....         | 76.73  |
| Hydrogen .....           | 41 | .... | 41  | .... | 11.88  | ....         | 11.89  |
| Oxygen .....             | 5  | .... | 40  | .... | 11.60  | ....         | 11.38  |
| <hr/>                    |    |      |     |      |        |              |        |
| Hydrated oleic acid .... | 1  |      | 345 |      | 100.00 |              | 100.00 |

Oleic acid is colorless, it has a slight odor, a somewhat acrid taste, and strongly reddens litmus; it is insoluble in water, but abundantly soluble in alcohol. It is decomposed when subjected to distillation, yielding sebacic acid, carbonic acid, and a peculiar hydrocarbon, together with a carbonaceous residue. Subjected to dry distillation with lime, (oleate of lime) it yields *oleone* ( $C_{42}H_{40}O_2$ ) in the form of an oily liquid, and a residue of carbonate of lime. (BUSSY.) It is energetically acted upon by nitric acid, and the products vary with the quantity and strength of the acid used, and the temperature; one of the results is a peculiar fatty acid; a volatile product similar to that obtained with stearic acid is also formed\*. When nitrous acid vapor is passed through oleic acid, it gradually forms a concrete compound of elaidic acid, combined with a peculiar red oily body containing nitrous acid, readily soluble in alcohol and ether, and forming blood-red compounds with the alkalis. (VARRENTRAPP.) According to Gottlieb, (*Ann. der Pharm.*, LVii. 52,) the red product arises from impurity, and the result of the action of nitrous acid on pure oleic acid is only elaidic acid. According to Boudet the action of sulphurous acid upon oleic acid resembles in its results that of nitrous acid, but is more feeble.

*Salts of the oleic acid.* Oleic acid expels carbonic acid from the carbonates. The neutral oleates contain 1 atom of basis combined with 1 of acid; they have little tendency to crystallize. The soluble alkaline oleates are soft fusible compounds, more soluble in alcohol than in water, and are decomposed by excess of water into free alkali and acid compounds. (CHEVREUL.)

\* According to Laurent and Bromeis, by the protracted action of nitric acid upon oleic acid, a clear solution is obtained, containing *suberic*, *pimelic*, *adipic*, and *azoleic* (œnanthyl?) acids. *Pimelic acid* (from *πιμελη*, *fat*,) crystallizes on evaporation, after the removal of the suberic acid, in hard granular crystals, fusible and volatile,

$= C_7H_5O_3, HO$ . The mother-liquor then yields *adipic acid* in radiated masses,  $= C_6H_4O_3, HO$ , and *lipic acid* (*λίπος*, *fat*) in tabular crystals,  $= C_5H_3O_4, HO$ . *Azoleic acid* is described by Laurent as an oily liquid, but Bromeis considers its definite character as doubtful. All these statements require verification.

*Oleate of Ammonia*,  $\text{NH}_4 \text{O}, \overline{\text{Ol}}$ , is a gelatinous compound, soluble in water; its solution becomes turbid, and evolves ammonia when heated.

*Oleate of Potassa*,  $\text{KO}, \overline{\text{Ol}}$ , is formed by heating equal parts of oleic acid and caustic potassa, with 5 parts of water; the resulting compound is subjected to pressure, and dissolved in alcohol; on evaporating the filtered solution, the pure oleate remains in the form of a deliquescent gelatinous soap, which, when carefully dried, becomes white and friable; it forms a ropy mixture with water, and is soluble in ether. When a concentrated aqueous solution of this neutral oleate is agitated with an additional equivalent of oleic acid, a gelatinous *binoleate of potassa* ( $\text{KO}, 2\overline{\text{Ol}}$ ) is formed; it is insoluble in water, but soluble in alcohol. (CHEVREUL.)

*Oleate of Soda*,  $\text{Na O}, \overline{\text{Ol}}$ , is obtained as the potassa salt; it absorbs moisture from the atmosphere, but does not deliquesce. It is soluble in 10 parts of water at  $90^\circ$ , and in 10 of alcohol, sp. gr. 0.821. (CHEVREUL.)

*Oleate of Baryta*,  $\text{Ba O}, \overline{\text{Ol}}$ , when dry, is a transparent yellowish salt, brittle when cold, but tough when warm, and attracts moisture when exposed to air. It contains 18.34 *per cent.* of baryta. (VARRENTRAPP.)

*Oleate of Lead*. When oleic acid is boiled with excess of liquid subacetate of lead, a fusible *basic oleate of lead*,  $= 2\text{Pb O}, \overline{\text{Ol}}$ , falls.

*Oleate of Silver*,  $\text{Ag O}, \overline{\text{Ol}}$ , falls in the form of a bulky white precipitate on mixing solutions of oleate of soda and nitrate of silver; if washed with warm water it loses its flocculent character, and acquires the consistence of plaster. It contains from 27 to 29 *per cent.* of oxide of silver. (VARRENTRAPP.)

OLEINE. *Oleate of Glycerine*. Oleine has already been mentioned as associated with margarine and stearine, in fats and oils; it is the leading ingredient in the greater number of the oils which remain fluid at common temperatures, and it is supposed that the properties of the greasy and of the drying oils are principally referable to peculiarities in their respective oleines, but perfectly pure oleine has not been obtained. It is procured in a state approaching to purity, by separating, as far as possible, the margarine and stearine from a fat oil, by cold and pressure, dissolving the liquid portion in ether, evaporating, and digesting the residue in cold alcohol, which dissolves the oleine, and leaves the greater part of the remaining margarine and the stearine undissolved. Kerwyk digests pure olive oil for 24 hours with about half the quantity of a solution of caustic soda which is requisite for its solution; the stearine and margarine are thus saponified, while the greater part of the oleine remains unaltered: on digesting the resulting mass in weak alcohol the soap dissolves, whilst the greater part of the oleine collects upon the surface. (LÖWIG.)

Oleine is colorless, inodorous, and tasteless; its specific gravity is about 0.9. The more it is free from stearine and margarine, the lower the temperature at which it congeals. It is insoluble in water, but abundantly soluble in alcohol and in ether. Subjected to dry distillation it yields sebacic acid and acroleine; when long exposed to air it gradually thickens, absorbing oxygen and evolving carbonic acid. With sulphuric acid it forms *sulpholeic acid*.



**ELAIDINE.** The action of nitrous acid, hyponitrous acid, and of nitrate of mercury, upon certain oils, has already been mentioned as producing a peculiar solid fatty matter. (BOUDET, *Ann. Ch. et Ph.*, L. 391.) This substance is best obtained by agitating olive oil with a mixture of nitrous acid with nitric acid. For this purpose 1 part of nitrate of lead may be heated in a retort connected with a receiver containing 1 part of nitric acid, sp. gr. 1·35. 10 parts of the mixed acid thus obtained is then agitated with 100 parts of olive oil till it begins to concrete; it is then set aside, and it gradually hardens into a yellow mass, which is to be heated with alcohol of the sp. gr. 0·833, and when cold, subjected to strong pressure between folds of bibulous paper. Thus purified, elaidine much resembles stearine in appearance; it fuses at about  $100^{\circ}$ ; it is almost insoluble in alcohol, but soluble in all proportions in ether. When heated in a retort it evolves acroleine, and a liquid passes over which concretes on cooling, assuming the appearance of butter, and consisting chiefly of elaidic and sebacic acid. When 4 parts of elaidine, 1 of caustic soda or potassa, and 2 of water, are heated together, glycerine is separated, and a soapy compound formed which, decomposed by hydrochloric acid, yields elaidic acid.

*Elaidic Acid* is soluble in alcohol and in ether, and may be obtained in the form of a white crystalline solid, by the evaporation of the former solution. It decomposes the alkaline carbonates, forming soluble elaidates of potassa and of soda, from which, by double decomposition, the insoluble elaidates may be prepared. Elaidic acid has, according to Gottlieb, the same elementary composition as oleic acid, being  $C_{36}H_{34}O_3, HO$ ; elaidine and oleine are therefore also probably isomeric. Exposed to air, elaidine becomes rapidly oxidized so as to form an oxyelaidic acid,  $= C_{36}H_{34}O_8$ , whilst oleic acid, under the same circumstances, gradually passes into  $C_{36}H_{34}O_5$ . (GOTTLIEB.)

**SEBACIC ACID** was discovered in 1799, by Thenard. (*Ann. de Chimie*, xxxix. 193.) Berzelius considered it as identical with benzoic acid (*Lehrbuch der Chemie*), but Dumas and Peligot subjected it to analysis in 1834 (*Ann. Ch. et Ph.*, lvii. 332), and proved it to be a distinct body. It is obtained by distilling tallow, agitating the product in boiling water, and adding acetate of lead, which throws down *sebate of lead*; this, washed, dried, and decomposed by dilute sulphuric acid, yields a solution of sebacic acid, which crystallizes on evaporation and cooling. When duly purified, it forms pearly acicular crystals, almost insipid, but reddening litmus paper. It is much more soluble in hot than in cold water, and very soluble in alcohol. When heated, it volatilizes like benzoic acid. Its formula is  $C_{10}H_{8}O_3, HO$ ; the equivalent of the anhydrous acid being 92. The ultimate components of the crystallized acid are

|                           |    |     |     |     |       | Dumas and Peligot. |       |
|---------------------------|----|-----|-----|-----|-------|--------------------|-------|
| Carbon .....              | 10 | ... | 60  | ... | 59·4  | ...                | 60·4  |
| Hydrogen.....             | 9  | ... | 9   | ... | 8·9   | ...                | 9·0   |
| Oxygen.....               | 4  | ... | 32  | ... | 31·7  | ...                | 30·6  |
| <hr/>                     |    |     |     |     |       | <hr/>              |       |
| Crystallized sebacic acid | 1  |     | 101 |     | 100·0 |                    | 100·0 |

The *sebates* of *ammonia*, *potassa*, and *soda*, are soluble; those of *lead*, *mercury*, and *silver*, are insoluble. (DUMAS.)

## § IX. VEGETABLE ACIDS.

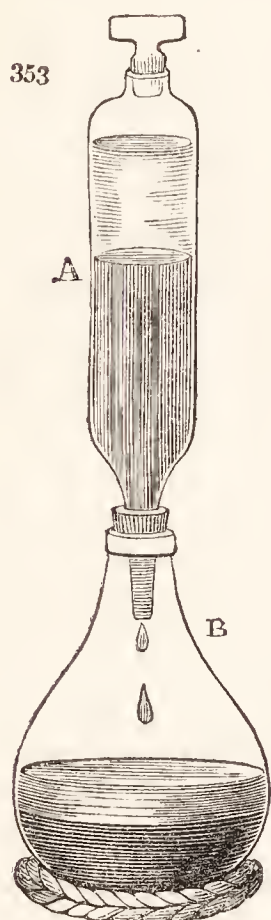
THIS section will include an account of some of the principal organic acids, and more especially of those which are found in vegetables, in a free or uncombined state. Several organic acids have been already adverted to; there are many others which are either limited to a few particular plants, or are only found in combination with organic alkaline bases, while others are chiefly known as connected with the products of fermentation, and others as belonging to peculiar secretions; these, together with certain other acids exclusively of animal origin, will be considered in subsequent sections.

I. TANNIC ACID. *Tannine. Quercitannic Acid.*  $C_{18}H_8O_{12}$ , =  $\overline{Tn}$ . There are many vegetable substances containing a principle which confers upon them an *astringent taste*, and which has the property of forming a precipitate in a solution of gelatine, and of striking a dark-blue or black precipitate with solutions of the persalts of iron. These properties are possessed in a remarkable degree by an infusion of *gall nuts*, those excrescences, which form upon the branches and shoots of the *Quercus infectoria*, being produced by the puncture of the female of the *Cynips gallæ tinctoriæ*, which insect deposits its ovum in the puncture, and occasions the excrescence, or gall, within which the larva is developed, and when the insect is perfect, it eats its way out. The best galls, known in commerce as *black* or *blue galls*, are gathered before the insect has escaped; the *white galls* are those from which the insect has departed, and are consequently perforated with a small circular hole. They are of a brownish or dingy-yellow color, and larger than the blue galls, but less heavy and less astringent. Gall-nuts are chiefly imported from Turkey; they were used in medicine in the time of Hippocrates, and have also been very long known as sources of *black dye*, and employed in the manufacture of *writing ink*. The first attempt at their chemical analysis was made about the middle of the last century by Dr. Lewis (*Philosophical Commerce of the Arts*), who detected in them a substance which “coagulates with isinglass, and blackens solutions of iron.” Deyeux regarded their active principle as a resin (*Journ. de Phys.*, xlii. 401.) Seguin was probably the first who accurately determined the nature of its action upon solutions of gelatine, and upon the skins of animals, and who applied the generic term *tannine* to this principle, as existing in a variety of substances employed in the conversion of skins into leather. (*Ann. de Chim.*, xx. 38.) Proust first attempted to obtain tannine in a pure and separate state, (*Ann. de Chim.*, xxv. 225,) and Davy determined its relative quantity in a variety of tanning materials. (*Phil. Trans.*, 1803.) But it was not till 1834 that we became acquainted with tannine or tannic acid, in its pure state, when a mode of separating it was pointed out by Pelouze, which enabled him to examine its properties, and ascertain its composition. (*Ann. Ch. et Ph.*, liv. 337; see also LAMBERT, *Journ. de Pharm.*, iv. 65.)

Pelouze's process is as follows. A glass vessel similar to that represented by A (fig. 353) is fitted into a flask, B; the upper vessel is about half filled with powdered galls, a small plug of cotton being placed at its



lower conical end to prevent the powder falling through: *washed ether* (that is, ether containing about a tenth part of water) is then poured upon the powder of galls, so as to soak into it, and fill the vessel, which is



then loosely stopped, and the ether is allowed slowly to filter through the powder into the vessel B, where the liquor separates into two strata, the lowermost of which is a concentrated aqueous solution of tannine, the uppermost being ether, holding a little tannine and gallic acid in solution. These liquors are separated, and the lowermost, after having been agitated or washed with some *pure ether*, is evaporated in vacuo over sulphuric acid; aqueous and ether vapor pass off, and the pure tannine is obtained in the form of a bulky pale-yellow residue. According to Pelouze, the tannine of the gall-nut is more soluble in water than its other constituents, so that it abstracts the water from the (washed) ether, and forms with it the lower stratum of liquid, upon which the ether itself floats. When the powder of gall-nuts is treated with pure and anhydrous ether, a magma is formed, and no fluid separates; but according to Guibourt (*Revue Scientif.*, ix. 32,) the presence of a little alcohol in the ether facilitates the process. The directions, however, as above given, answer very well; and although

other processes have been suggested by Berzelius, (*Lehrbuch*,) Cadet, (*Ann. Ch. et Ph.*, iv. 405,) Dominé, (*Journ. de Pharm.*, 1844, i. 231,) and others, that of Pelouze appears, upon the whole, to be the simplest and most effectual.

Pure tannic acid is nearly colorless; it is inodorous, pre-eminently astringent in taste, uncrystallisable, very soluble in water, and less soluble in pure alcohol and ether. Its aqueous solution reddens litmus, and decomposes the alkaline carbonates with effervescence. It combines energetically with gelatine: when, therefore, a piece of skin or bladder is immersed in its aqueous solution, the tannic acid is entirely abstracted; whereas if *gallic acid* were present, that acid remains dissolved in the water. Tannic acid also furnishes an abundant white precipitate in solutions of isinglass or of glue. A concentrated aqueous solution of tannic acid is precipitated by hydrochloric, nitric, sulphuric, phosphoric, and arsenic acid; but not by oxalic, tartaric, lactic, acetic, or citric acid. By the prolonged action of acids and alkalis, tannic acid undergoes various and often complicated changes, amongst which its conversion into gallic acid is most common.

Tannic acid has been analyzed with the following results:—

|              |       |     |       |     |        | Berzelius. |        | Liebig. |        | Pelouze. |        |
|--------------|-------|-----|-------|-----|--------|------------|--------|---------|--------|----------|--------|
| Carbon ..... | 18    | ... | 108   | ... | 50.94  | ...        | 52.69  | ...     | 52.51  | ...      | 51.77  |
| Hydrogen ... | 8     | ... | 8     | ... | 3.77   | ...        | 3.86   | ...     | 4.12   | ...      | 3.98   |
| Oxygen ..... | 12    | ... | 96    | ... | 45.29  | ...        | 43.45  | ...     | 43.37  | ...      | 44.25  |
| <hr/>        | <hr/> |     | <hr/> |     | <hr/>  |            | <hr/>  |         | <hr/>  |          | <hr/>  |
| Tannic acid  | 1     |     | 212   |     | 100.00 |            | 100.00 |         | 100.00 |          | 100.00 |

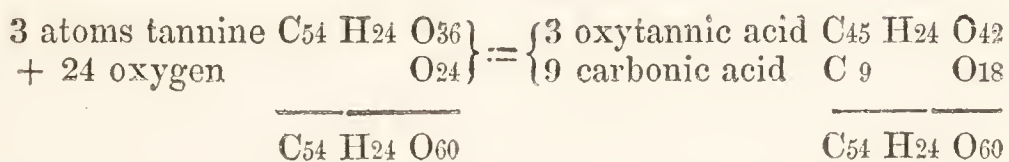
According to Berzelius and Pelouze, tannic acid is *anhydrous*, and they represent the tannate of lead, dried at 120°, as = PbO, C<sub>18</sub> H<sub>8</sub>



O12. Liebig, by adding tannic acid to an excess of a hot solution of acetate of lead, obtained a salt which he represents as  $= 3 \text{ PbO}, \text{C}_{18} \text{H}_5 \text{O}_9$ ; he therefore regards the tannic acid as *tribasic*, and represents the isolated acid by the formula  $\text{C}_{18} \text{H}_5 \text{O}_9 + 3 \text{HO}$ . Löwig regards the tannic acid as monohydrated, and represents it as  $\text{C}_{18} \text{H}_7 \text{O}_{11} + \text{HO}$ , a formula, he observes, consistent with all its salts, with the exception of Liebig's tannate of lead.

When a solution of tannic acid is exposed to air, it gradually loses its transparency, and deposits a grey crystalline powder, which is *gallic acid*; during this change oxygen is absorbed, and an equal volume of carbonic acid evolved, but the whole of the tannic acid is never thus converted; and Robiquet found that, after eight months' exposure, half of the tannic acid remained unchanged. (*Ann. Ch. et Ph.*, XLIV. 385.) When a dilute solution of tannic acid is precipitated by dilute sulphuric acid, and the mixture boiled for a few minutes, it deposits crystals of gallic acid on cooling; but when it is acted on by concentrated sulphuric acid, it is only partly converted into gallic acid, and partly into a brown substance, having the characters of *humic acid*. By the action of nitric acid, tannine yields oxalic acid, and nitrous gas is evolved.

The decomposition of tannine by the alkalis has been examined by Büchner. (*Ann. der Pharm.*, LIII. 357.) When a moderately strong solution of tannic acid in caustic potassa is exposed in a shallow vessel to the air, the liquor becomes first yellow, then red, and after some days, almost opaque, in consequence of the formation of what he terms *oxytannic acid*, and of carbonic acid.



*Tannate of Ammonia* is formed by passing gaseous ammonia into a solution of tannic acid in absolute alcohol; it falls in white flakes; if the alcohol be hydrated, it assumes an oily appearance. The analysis of this compound, however, shows that the tannine is changed in ultimate composition. (BÜCHNER.)

*Tannate of Potassa* is formed by adding solution of tannic acid to a solution of pure potassa, or of its carbonate or bicarbonate. It is difficultly soluble in water and in alcohol. In the state of *hydrate*, it is white and gelatinous; when *dry*, it has an earthy aspect, an astringent taste, and no alkaline reaction on vegetable colors. (BERZELIUS.)

*Tannate of Soda* is more soluble than the potassa salt; and it forms a yet more soluble basic salt, which has a slight alkaline reaction, and yields yellow crystalline films on spontaneous evaporation.

*Tannate of Lime*. The basic salt is insoluble; the neutral salt sparingly soluble in water, and also in weak alcohol.

*Tannate of Baryta* is very sparingly soluble in water; it is more soluble in excess of tannic acid, and in acetic acid. The salt of *strontia* resembles it.

*Tannate of Magnesia*, obtained by digesting magnesia in a solution of tannic acid, is a difficultly soluble basic salt.

*Tannates of Iron*. No precipitate is occasioned by adding a dilute



solution of tannic acid to the pure *protosalts* of iron; when both solutions are concentrated, a white gelatinous precipitate falls. When a solution of tannic acid is dropped into a solution of persulphate of iron, no change is at first perceived, inasmuch as the peroxide is reduced by the tannic acid to the state of protoxide; but on adding excess of tannic acid a black precipitate falls, consisting of that acid combined with peroxide and protoxide of iron. The same precipitate is also formed when tannic acid is added to a solution of the sulphate of protoxide of iron and the mixture exposed to air. (BARRESWILL.) According to Pelouze, the black precipitate consists of 1 atom of peroxide of iron and 3 of tannic acid  $= \text{Fe}_2\text{O}_3 + 3[\text{C}_{18}\text{H}_8\text{O}_{12}]$ . When boiled with water, carbonic acid is evolved, and it loses color. Water, which merely holds in solution a trace of peroxide of iron, acquires a fine blue tint on the addition of tannic acid. The pertannate of iron (mixed with a little gallate,) is the coloring matter of common writing ink, its deposition in the form of a precipitate being there to a great extent prevented by gum or some other viscid substance\*.

\* In making good *Writing Ink*, the great object is to regulate the proportion of sulphate of iron to the galls. If it be in excess, although the ink may at first appear black, it becomes subsequently brown and yellow. Hence, some time should elapse before ink is used after the ingredients are put together, in order to be tested from time to time, and the combinations perfectly regulated. Gum is added to retain the coloring matter in suspension, to prevent too great fluidity in the writing, and to protect the vegetable matter from decomposition. Logwood, and other vegetable astringents, have been tried for atramental purposes, but do not yield a permanent ink.

An excellent ink is obtained as follows, but, if the paper has been made from inferior rags, bleached by an excess of chlorine, ink, however good, will be ultimately discolored.

Aleppo galls finely bruised 6 oz., crystallized sulphate of iron 4 oz., gum-arabic 4 oz., water 6 pints. Boil the galls in the water, then add the other ingredients, and keep the whole in a wooden or glass vessel, occasionally shaken. In two months, strain, and pour off the ink into glass bottles, to be well corked. To prevent mould, add one grain of corrosive sublimate, or three drops of kreasote to each pint of ink. Sulphate of copper is occasionally added to ink, but is rather injurious than otherwise.

*Ink powder* is a mixture of 12 ounces of powdered galls, 4 ounces of pulverized and dried sulphate of iron, and 1 ounce of gum-arabic. 1 ounce of this powder, infused in a pint of boiling water, produces a pint of ink. All the *tannoferric inks* are liable to fade with age, and ultimately become ille-

gible, or leave only a slight ferruginous stain in the paper or parchment which has been written upon. In these cases the writing may generally be restored by washing it first with a weak solution of oxalic or hydrochloric acid, and then applying an infusion of galls. The great merit of these inks consists in the facility of their preparation, the ease with which they flow from the pen, and the manner in which they bite into the paper, so as not to be easily removed by sponging. The merit of *carbonaceous inks*, such as *China* or *Indian ink*, has been already noticed, but there is often much difficulty in getting a *vehicle* well adapted to their preparation. According to Professor Traill, an acetic solution of gluten forms an excellent basis of a durable and indelible writing ink. The gluten is obtained in the usual way by kneading the dough of wheat-flour in a stream of water till the starch is perfectly separated; the gluten should be kept from 24 to 36 hours in water, and then digested in acetic acid of the specific gravity 1.033 to 1.034, in the proportion of 3 parts of gluten to 20 parts of the acid. By the aid of a gentle heat, a greyish-white saponaceous fluid is obtained, which will keep for a long time. The coloring matter should consist of from 8 to 12 grains of the best lamp black, and two grains of indigo, thoroughly incorporated with each fluid ounce of the vehicle. An agreeable aroma may be communicated by digesting bruised cloves, pimento, or cinnamon, in a portion of the original acid. This ink may be used with a steel pen, which however should not be left in it, and should be washed after use: it is not calculated for writing on parchment. (*Edinb. Phil. Trans.*, xiv. 427.)

*Tannate of Lead* is thrown down in the form of a white flocculent precipitate on adding tannic acid to a solution of acetate of lead; if the precipitate be boiled in the solution of the acetate, a yellow powder is obtained =  $3\text{PbO}, \text{C}_{18}\text{H}_5\text{O}_9$ . (LIEBIG.)

*Tannate of Antimony.* When a solution of tannic acid is added to one of emetic tartar, a white gelatinous precipitate falls, and a compound of tannine and bitartrate of potassa remains in solution. The precipitate is =  $\text{Sb}_2\text{O}_3, \text{C}_{18}\text{H}_8\text{O}_{12}$ . (PELOUZE.) It is in reference to this action, that vegetable infusions containing tannine, are used as antidotes in cases of poisoning by emetic tartar.

The compounds of tannic acid with *proteine* and with *gelatine*, have been above adverted to.

An *infusion of galls* occasions precipitates in the greater number of metallic solutions, the characters and colors of which are sometimes resorted to as indications of the oxide present. In the following table, the metal and the solution employed are indicated in the first and second columns, and the color of the precipitate in the third and fourth: the third column gives the results of my own trials, and the fourth those of Dumas. It may be observed, that discrepancies arise in this case from the strength of the metallic solution, and also from its acid or basic character, so that neutral solutions should as far as possible be used.

TABLE OF METALLIC PRECIPITATES BY A STRONG INFUSION OF GALLS.

| METAL.        | SOLUTION.                        | PRECIPITATE.        |              |
|---------------|----------------------------------|---------------------|--------------|
| MANGANESE     | Neutral protochloride            | Dirty-yellow        | 0            |
| IRON.....     | Neutral protosulphate            | Purple tint         | 0            |
| Ditto.....    | Persulphate                      | Black               | Blue-black   |
| ZINC.....     | Chloride                         | Dirty-yellow        | 0            |
| TIN .....     | Acid protochloride               | Straw colour        | Yellowish    |
| Ditto.....    | Acid perchloride                 | Fawn colour         | Ditto        |
| CADMIUM.....  | Chloride                         | ?                   | 0            |
| COPPER .....  | Protochloride                    | Yellow-brown        | ?            |
| Ditto.....    | Nitrate                          | Green               | Gray         |
| LEAD .....    | Nitrate                          | Dingy-yellow        | White        |
| ANTIMONY .... | Tartrate of antimony and potassa | Straw-colour        | White        |
| BISMUTH ..... | Tartrate of bismuth and potassa  | Yellow, and copious | Orange       |
| COBALT .....  | Chloride                         | 0                   | Yellow-white |

A *blue writing fluid* has been introduced, the coloring matter of which is said to be sulphate of indigo and tannogallate of iron. Mr. Stephens has also patented a blue ink,

the coloring matter of which is Prussian-blue dissolved in water by means of oxalic acid.



TABLE OF PRECIPITATES BY INFUSION OF GALLS.

| METAL,         | SOLUTION,                 | PRECIPITATE.         |               |
|----------------|---------------------------|----------------------|---------------|
|                |                           |                      |               |
| URANIUM.....   | Sulphate                  | Dark-brown           | Reddish-brown |
| TITANIUM ....  | Acid hydrochlorate        | Brown-red            | Blood-red     |
| Ditto .....    | Neutral sulphate          | Blood-red            | Ditto         |
| CERIUM .....   | Sulphate                  | Yellowish            | Yellow        |
| TELLURIUM .... | Chloride                  | Yellow               | Yellow        |
| ARSENIC .....  | White oxide               | Little change        | ?             |
| Ditto .....    | Arsenic acid              | 0                    | ?             |
| MOLYBDENUM     | Chloride                  | Brown                | Brown         |
| NICKEL .....   | Sulphate                  | Green                | Yellow-green  |
| MERCURY ....   | Acid protonitrate         | Yellow               | ?             |
| Ditto.....     | Acid perntrate            | Yellow               | ?             |
| Ditto.....     | Corrosive sublimate       | 0                    | ?             |
| OSMIUM .....   | Aqueous solution of oxide | Purple becoming blue | Bluish-purple |
| RHODIUM.....   |                           |                      |               |
| PALLADIUM....  |                           |                      |               |
| SILVER.....    | Nitrate                   | Curdy and brown      | Dirty-yellow  |
| GOLD .....     | Perchloride               | Deep-brown           | Brown         |
| PLATINUM ....  | Protochloride             | Brownish-green       | Dark-green    |

II. GALLIC ACID. *G.* This acid was discovered by Scheele, (*Stockholm Transactions*, 1786, and *Opuscula*, ii. 224,) and modes of obtaining it were afterwards suggested by Deyeux, (*Crell's Annals*, i. 29,) and by Braconnot, (*Ann. Ch. et Ph.*, ix. 181,) by Liebig, (*Ann. der Pharm.*, xxvi. 126,) and by Stenhouse, (*ibid.* xlv., i. and *Mem. Chem. Soc.*, i. 126.) The conversion of tannic into gallic acid by the agency of oxygen was first demonstrated by Pelouze, (*Ann. Ch. et Ph.* liv. 337, lvii. 423,) and the presence of gallic, independent of tannic acid, in several vegetables, has been proved by Stenhouse, and by Robiquet. (*Journ. de Pharm.*, Sept., 1836.)

Gallic acid may be obtained, (1,) by mixing powdered galls with water, and exposing the paste for some weeks to the air, at a temperature of 70° to 75°, occasionally adding water to prevent desiccation; the powder swells, and becomes mouldy, and when the magma is subjected to pressure, a quantity of colored liquid may be squeezed out; the residue, or cake, is then boiled in water, and the solution filtered while hot; on cooling it deposits crystals of gallic acid, which may be purified by re-dissolving, and boiling with a little animal charcoal; the filtered solution then deposits the gallic acid in the form of white silky crystals. (BRACONNOT.) (2.) A concentrated cold infusion of gall-nuts is precipitated by sulphuric acid; the precipitate is first washed with very dilute sulphuric acid, pressed out, and then dissolved in a diluted sulphuric acid, composed

of 1 part of acid and 2 of water, and boiled for some minutes; on cooling, it deposits crystals which are to be purified by a second crystallisation, dissolved in hot water, and precipitated by acetate of lead; the precipitated gallate of lead is then well washed, diffused in boiling water, and decomposed by a current of sulphuretted hydrogen; colorless crystals of gallic acid are deposited as the filtered liquor resulting from this operation cools.

Gallic acid crystallises in long silky needles of a slightly sour and astringent taste, soluble in about 100 parts of cold and in 3 of boiling water; readily soluble in alcohol, and sparingly soluble in ether: it occasions no precipitate with gelatine. The formula of the crystals is variously represented, in reference to their constituent water; they are probably  $C_7H_3O_5 + HO$ , their equivalent being 94; the acid dried at  $212^\circ$  contains,—

|                           |     |     |    |        | Pelouze. | Liebig. | Stenhouse. |        |        |        |        |
|---------------------------|-----|-----|----|--------|----------|---------|------------|--------|--------|--------|--------|
| Carbon .....              | 7   | ... | 42 | ...    | 49.41    | ...     | 50.10      | ...    | 49.85  | ...    | 49.49  |
| Hydrogen .....            | 3   | ... | 3  | ...    | 3.53     | ...     | 3.64       | ...    | 3.48   | ...    | 3.53   |
| Oxygen .....              | 5   | ... | 40 | ...    | 47.06    | ...     | 46.26      | ...    | 46.67  | ...    | 46.98  |
| <hr/>                     |     |     |    |        |          |         |            |        |        |        |        |
| Gallic acid dried at 212° | ... | 1   | 85 | 100.00 | 100.00   | 100.00  | 100.00     | 100.00 | 100.00 | 100.00 | 100.00 |

But it is probable that the acid dried at  $212^\circ$  still retains an atom of water, being  $= C_7H_2O_4 + HO$ .

According to Liebig, gallic acid is *bibasic*, and represented by the formula  $C_7H_2O_4 + 2HO$ .

The basic salts of the gallic acid when exposed to air, absorb oxygen, and acquire various shades of yellow and brown, till they ultimately blacken, in consequence of the formation of *Tanno-melanic acid*  $= C_{14}H_4O_7 + 2HO$ . (BÜCHNER, *Ann. der Pharm.*, liii. 373.)

*Gallate of Ammonia* is obtained in the form of a white crystalline powder, by passing gaseous ammonia into an alcoholic solution of gallic acid; when dissolved in a small quantity of boiling water, it forms yellowish crystals as the liquor cools: these crystals lose no water by drying at  $212^\circ$ : their formula, according to the analysis of Büchner, appears to be either  $NH_4O, + 2[C_7H_2O_4 + HO]$  or  $[NH_4O, HO, C_7H_2O_4] + C_7H_2O_4, 2HO$ .

*Gallate of Potassa*. When an alcoholic solution of potassa is dropped into an alcoholic solution of gallic acid till green streaks remain upon the surface, a white crystalline precipitate forms, which acquires a greenish hue by exposure to air, and becomes brown when dissolved in water; it loses no weight when dried at  $212^\circ$ , and appears, from the analysis of Büchner, to be  $= KO, + 3(C_7H_2O_4)$ . The same compound is formed when *tannic acid* is gradually added to a boiling solution of caustic potassa as long as effervescence ensues, then supersaturated with acetic acid, and the resulting crystalline mass treated by boiling alcohol; the *acid gallate of potassa* remains. (BÜCHNER.)

*Gallate of Soda* is obtained by a process similar to the preceding, in the form of a white crystalline powder, forming a brown solution. At  $212^\circ$  this salt loses 22 per cent.  $= 6$  atoms of water. The anhydrous salt is  $[NaO, C_7H_2O_4] + C_7H_2O_4$ , and the crystallised,  $NaO, 2[C_7H_2O_4] + 5HO$ .

*Gallate of Lime*. When solutions of gallate of potassa and chloride



of calcium are mixed, a greenish brown precipitate falls, which is increased in quantity by the addition of ammonia. This salt may also be obtained by adding freshly precipitated carbonate of lime to a boiling solution of gallic acid, as long as effervescence ensues, then diluting with water, boiling for a few minutes, filtering, and evaporating; small acicular crystals and white saline crusts are deposited, difficultly soluble in water, and not losing weight when dried at  $212^{\circ}$ . They are  $\text{CaO}, 2[\text{C}_7\text{H}_3\text{O}_5] + 2\text{HO}$ . (BÜCHNER.)

*Gallate of Baryta* may be obtained as the lime salt: the crystals lose no water at  $212^{\circ}$ : they are  $\text{BaO}, 2(\text{C}_7\text{H}_3\text{O}_5) + 2\text{HO}$ .

*Gallates of Magnesia*. Büchner has described four definite compounds of gallic acid and magnesia.

*Gallate of Manganese*, is thrown down in the form of a heavy white crystalline precipitate on adding a concentrated solution of acetate of manganese to a hot saturated solution of gallic acid; when well washed, and dried out of contact of air, it acquires a yellow tint: its formula, derived from Büchner's analysis, is  $7\text{MnO}, 6[\text{C}_7\text{H}_3\text{O}_5] + 4\text{HO}$ .

*Gallate of Iron*. When gallic acid is added to cold solutions of the persalts of iron, they acquire a dark blue color, which disappears on the application of heat, the peroxide losing oxygen, and carbonic acid being evolved. The *gallate of protoxide of iron* is a soluble colorless compound, but it becomes red, violet, and finally dark blue, by absorption of oxygen, still however remaining soluble, till at length it blackens and is precipitated: it is then a *gallate of the black, or deutoxide of iron*, and may be at once formed by adding gallic acid to a solution of that oxide. It forms a part of the coloring matter of writing ink. If a solution of it in hydrochloric acid be agitated with ether, it abstracts the gallic acid, which may be obtained crystallised on evaporation.

*Gallate of Lead*. When acetate of lead is added to a hot solution of gallic acid, leaving the latter in excess, a grey crystalline powder falls =  $2\text{PbO}, \text{C}_{14}\text{H}_5\text{O}_9 = \text{PbO}, \text{C}_7\text{H}_2\text{O}_4 + \text{PbO}, \text{C}_7\text{H}_3\text{O}_5$ . When this compound is dried between  $212^{\circ}$  and  $300^{\circ}$ , it loses an atom of water, and is then  $\text{PbO}, \text{C}_7\text{H}_2\text{O}_4$ . (BÜCHNER.) When a solution of gallic acid is added to a boiling solution of acetate of lead, so as to leave the latter in excess, a yellow crystalline basic gallate falls =  $2\text{PbO}, \text{C}_7\text{H}\text{O}_3$ . (LIEBIG.)

*Gallate of Antimony*. Gallic acid and the alkaline gallates, throw down a white precipitate from solution of emetic tartar, containing about 43 per cent. of oxide of antimony.

III. ELLAGIC ACID. This term (derived from the word *galle*, read backwards,) has been applied by Braconnot, (*Ann. Ch. et Ph.*, ix. 181,) to a substance produced along with gallic acid, by the exposure of moistened galls to air. It seems first to have been observed by Chevreul. (*Ann. Ch. et Ph.*, ix. 329.) It is contained, according to Grischow, in the root of *Tormentilla erecta*, and it also appears to exist in the intestinal concretions termed *Oriental Bezoars*. (*Phil. Mag.*, May, 1844. *Ann. der Pharm.*, Aug. 1845.) Being insoluble in boiling water, it remains after the gallic acid has been extracted, and may be dissolved out of the residue by a very weak solution of potassa, from which dilute hydrochloric acid throws it down in the form of a tawny powder, tasteless, and almost insoluble in water, alcohol, and ether. It slightly red-

dens litmus. When a strong solution of potassa is dropped upon it, heat is produced, and it neutralizes the alkali, forming crystalline scales, insoluble in water, but soluble in excess of the alkali. The ammonia and the soda salt closely resemble the preceding. According to Pelouze, ellagic acid dried in the air, is  $\text{C}_7\text{H}_2\text{O}_4 + \text{H}_2\text{O}$ ; when dried at  $250^\circ$ , it is rendered *anhydrous*, and consists of

|                             |   |     |    |     |       | Pelouze. |
|-----------------------------|---|-----|----|-----|-------|----------|
| Carbon.....                 | 7 | ... | 42 | ... | 55.3  | 55.69    |
| Hydrogen .....              | 2 | ... | 2  | ... | 2.6   | 2.48     |
| Oxygen .....                | 4 | ... | 32 | ... | 42.1  | 41.83    |
| <hr/>                       |   |     |    |     |       |          |
| Anhydrous ellagic acid .... | 1 |     | 76 |     | 100.0 | 100.00   |

IV. PARAELLAGIC ACID. When gallic acid is heated to about  $285^\circ$  with sulphuric acid, and the resulting solution mixed with water, a red crystalline powder is deposited, which, when washed and dried, amounts to about one-half of the weight of the gallic acid employed. This product is almost insoluble in pure water: it forms a red soluble crystalline salt when saturated with potassa. Its ultimate components are the same as those of the ellagic acid. This, and the ellagic acid, are probably isomeric varieties of gallic acid.

V. PYROGALLIC ACID. Scheele first obtained this acid by sublimation from galls, and it was considered as identical with gallic acid. (*Opuscula*, ii. 224.) It was afterwards examined by Deyeux, (*Journ. de Physique*, xlii. 416,) and by Braconnot and Pelouze, (*Ann. Ch. et Ph.*, xlii. 206, liv. 337.) This acid may be obtained by heating gallic acid (previously dried at  $212^\circ$ ) in a small glass retort immersed in an oil bath, to a temperature between  $410^\circ$  and  $420^\circ$ . It sublimes in the form of white brilliant lamellar crystals; but it is apt to be contaminated by empyreumatic oil, and may be more economically procured as follows, (STENHOUSE, *Mem. Chem. Soc.*, i. 128): Finely powdered galls are treated with successive portions of cold water till exhausted, and the infusions carefully evaporated to dryness, when they leave a spongy deliquescent mass, which is to be pulverised and spread equally over the bottom of a cast iron pan, 3 or 4 inches deep, and about a foot in diameter, the top of which is covered with a diaphragm of bibulous paper, pasted round its rim, pierced with pin holes, and surmounted by a paper cap 12 to 18 inches high. The pan is then cautiously heated for 10 or 12 hours, so as to preserve its temperature as nearly as may be at about  $400^\circ$ . The crystals of pyrogallie acid collect in the cap, the other products being chiefly absorbed by the paper.

Pyrogallie acid is white, crystalline, inodorous, and bitter. When pure it does not redden litmus paper. It is very soluble in water, alcohol, and ether, and the aqueous solution, evaporated in vacuo, yields white acicular crystals, which are anhydrous, fusible at  $240^\circ$ , and sublime in the form of an acrid vapor at  $410^\circ$ . An aqueous solution of pyrogallie acid blackens on long exposure to air, and deposits a brown powder: it gives a deep indigo blue color, but no precipitate, with protosulphate of iron, which changes to dark green if peroxide be present; with persulphate of iron it gives an orange color, and red with perchloride of iron: dropped into milk-lime, a purple color appears, which



changes to brown. Chlorine colors the crystals of pyrogallie acid, first red and then black. Iodine has no effect upon them. This acid reduces the oxides of silver, gold, and platinum, and precipitates them completely in the metallic state. (STENHOUSE.)

The formula ascribed to pyrogallie acid by Berzelius, is  $C_6 H_3 O_3$ , which gives the equivalent 63. Stenhouse represents it as  $C_8 H_4 O_4$ , which produces the equivalent 84, the composition of *pyrogallate of lead* being  $Pb O, C_8 H_4 O_4$ . The following are the results of the analyses.

|                 |   |     |    |     | Berzelius. |     | Pelouze. |     | Liebig. |     | Stenhouse. |
|-----------------|---|-----|----|-----|------------|-----|----------|-----|---------|-----|------------|
| Carbon .....    | 6 | ... | 36 | ... | 57.14      | ... | 56.64    | ... | 57.61   | ... | 57.60      |
| Hydrogen ....   | 3 | ... | 3  | ... | 4.76       | ... | 5.00     | ... | 4.70    | ... | 4.78       |
| Oxygen.....     | 3 | ... | 24 | ... | 38.10      | ... | 38.36    | ... | 37.69   | ... | 37.62      |
| <hr/>           |   |     |    |     |            |     |          |     |         |     |            |
| Pyrogallie acid | 1 |     | 63 |     | 100.00     |     | 100.00   |     | 100.00  |     | 100.00     |

According to Berzelius, pyrogallie acid expels carbonic acid from the carbonates of the alkalis, but not of the earths. Pelouze describes the *pyrogallate of potassa* and *pyrogallate of soda* as crystallisable salts. According to Stenhouse, the alkaline pyrogallates cannot be obtained. When even a single drop of caustic ammonia is added to a solution of pyrogallie acid, it becomes dark brown and alkaline. On adding excess of ammonia to pyrogallie acid, and evaporating in vacuo, the acid crystallises in confused tufts of a brown color, but containing no ammonia. *Pyrogallate of lead* falls in the form of a copious white flocculent precipitate, on mixing cold solutions of pyrogallie acid and acetate of lead. When dried in vacuo, it gave 57.18 per cent. of oxide of lead. (STENHOUSE.)

VI. MELANOALLIC ACID. *Metagallie Acid*. When dry gallic acid is rapidly heated up to  $480^\circ$ , carbonic acid and water are evolved, and instead of a sublimate of pyrogallie acid, a black shining and tasteless substance is produced, which is insoluble in water, alcohol, and ether, but soluble in the alkalis, and again precipitated by acids in the form of a black powder. It expels carbonic acid from the alkaline carbonates, but not from carbonate of baryta: it is neutral to vegetable colors; it produces black precipitates in solutions of baryta, strontia, lime, magnesia, iron, zinc, lead, and copper. (PELOUZE. *Ann. Ch. et Ph.*, liv. 337.) Its formula appears to be  $C_{12} H_3 O_3, HO$ , and its equivalent 108. In combination, the equivalent of the acid is 99, its elements being

|                             |    |     |    |     | Pelouze. |
|-----------------------------|----|-----|----|-----|----------|
| Carbon.....                 | 12 | ... | 72 | ... | 72.72    |
| Hydrogen .....              | 3  | ... | 3  | ... | 3.04     |
| Oxygen .....                | 3  | ... | 24 | ... | 24.24    |
| <hr/>                       |    |     |    |     |          |
| Anhydrous melanogallie acid | 1  |     | 99 |     | 100.00   |
|                             |    |     |    |     | 100.00   |

VII. MELANOTANNIC ACID. This acid is formed when a solution of tannic or gallic acid, with excess of potassa, is heated in the contact of air, till it no longer affords a precipitate of gallic acid on being supersaturated with acetic acid; with which it is then evaporated to dryness, and the black residue washed with dilute alcohol to separate the acetate of potassa. The product is then dissolved in water, acidulated by acetic

acid, and precipitated by acetate of lead: a brownish black compound falls, which, when dried, assumes a pulverulent form, and is  $= 2\text{PbO}$ ,  $\text{C}_{14}\text{H}_4\text{O}_7$ . Büchner therefore represents the melanotannic acid by the formula  $\text{C}_{14}\text{H}_4\text{O}_7 + 2\text{HO}$ . (*Ann. der Pharm.*, liii. 373.)

In reference to the preceding statements respecting the composition of tannic acid and its derivatives, their composition stands as follows:

|                         |  |
|-------------------------|--|
| Tannic acid .....       | $\text{C}_{18}\text{H}_8\text{O}_{12}$ |
| Oxytannic acid .....    | $\text{C}_{15}\text{H}_8\text{O}_{14}$ |
| Melanotannic acid ..... | $\text{C}_{14}\text{H}_6\text{O}_9$    |
| Melanogallic acid ..... | $\text{C}_{12}\text{H}_3\text{O}_3$    |
| Gallic acid.....        | $\text{C}_7\text{H}_3\text{O}_5$       |
| Ellagic acid .....      | $\text{C}_7\text{H}_2\text{O}_4$       |
| Paraellagic acid .....  | $\text{C}_7\text{H}_2\text{O}_4$       |
| Pyrogallic acid.....    | $\text{C}_6\text{H}_3\text{O}_3$       |

VIII. MIMOTANNIC ACID. *Tannine of Catechu. Tanningenic Acid.* (BERZELIUS, *Lehrbuch*. PELOUZE.) The most direct process for obtaining this modification of tannic acid, consists in treating powdered catechu with hydrated ether in the same way as galls are treated in procuring gallic acid (p. 1286.) The liquor which passes through, but which does not, as in the other case, separate into two layers, when evaporated in vacuo, leaves the tannine. It is yellow, very astringent, and in its general characters resembles gall-nut tannine. When it is exposed in dilute aqueous solution to the action of air, it becomes brown, and a substance is then obtained on evaporation, which resembles the portion of the catechu which the ether does not dissolve. The principal peculiarities of this form of tannine are, that it gives a dirty green precipitate with the persalts of iron, and that it occasions no precipitate in a solution of emetic tartar. Löwig represents it as an inferior oxide of the same radical which forms the basis of gall-nut tannine.

|                            |  |
|----------------------------|--|
| Catechu tannine . . . . .  | $\text{C}_{18}\text{H}_8\text{O}_8$    |
| Gall-nut tannine . . . . . | $\text{C}_{18}\text{H}_8\text{O}_{12}$ |

IX. CATECHUIC ACID. *Catechine.* This substance (to which the name of *tanningenic acid* has also sometimes been applied) may be obtained as follows. *Bengal catechu*, commonly termed by tanners *Terra Japonica*, or *Gambier*, (the produce of *Nauclea* or *Uncaria Gambier*) and which occurs in commerce in small cubes of a dark brown externally and pale within, and of a dull porous fracture, is pulverised, and infused in repeated portions of cold water to wash out the tannine; the residue is then boiled in several portions of water, and these decoctions deposit impure catechuic acid as they cool, which after having been well edulcorated with cold water, is boiled with purified animal charcoal in 6 times its weight of water; the hot filtered liquor deposits the pure acid on cooling. (WACKENRODER, *Ann. der Pharm.*, xxxi. and xxxvii.) Zwinger and Hagen, have also given processes for its preparation, (*Ann. der Pharm.*, xxxvii. 336 and 320,) and Cooper has described it as collecting upon the surface of leather tanned by catechu. (*Mem. Chem. Soc.*, II. 45.)

Catechuic acid is white, and of a silky or micaceous aspect, forming,



when slowly deposited from a hot saturated solution in water or alcohol, groups of acicular crystals. It is very sparingly soluble in cold water, but it dissolves in about 4 parts of boiling water, and is only gradually deposited on cooling, or on diluting with cold water. It is soluble in about 6 parts of cold, and 3 of hot alcohol; and in 128 parts of cold, and 78 parts of boiling ether. It fuses when heated, and concretes on cooling into a brittle mass. Its aqueous solution does not precipitate gelatine: when heated up to somewhat above  $400^{\circ}$ , it is decomposed. The formula of catechuic acid deduced from the analyses of Svanberg, (*Poggend. Ann.*, xxxix. 167,) Zwinger, and Hagen, (see *Löwig*, ii. 740,) is, in its *anhydrous* state, (combined with oxide of lead,)  $C_{14}H_6O_6$ ; dried at  $212^{\circ}$ , it retains 1, and at  $60^{\circ}$  2 atoms of water.

When catechuic acid is subjected to dry distillation, it yields a crystalline product, which may be purified by sublimation, and which Zwinger has described under the name of *pyrocatechuic acid*  $= C_6H_2O + HO$ . When a solution of catechuic acid in carbonate of potassa is exposed to the air, it acquires a dark color, and passes, according to Svanberg, into *Rubinic acid*,  $C_{18}H_6O_9$ , and *Japonic acid*,  $C_{12}H_4O_4$ .

There are many other varieties of tannine, some of which, such as the *Kinotannic* and *Cinchonotannic acids*, seem to be peculiar. It is also found in many barks, as in that of the oak, larch, birch, &c.; in tea-leaves, and coffee-berries, and in a great number of other plants.

The relative proportions of tanning matter in different vegetables, may be tolerably well judged of by the weight of the precipitate which their infusions afford in a strong solution of isinglass. The following table, by Cadet, shows the relative weights of this precipitate formed by an infusion of 100 parts of the respective substances.

|  |    |  |    |
|--|----|--|----|
| Galls .....                            | 86 | Weeping-willow bark .....                | 16 |
| Tormentil root .....                   | 50 | Bohemia olive bark .....                 | 16 |
| Alder bark .....                       | 36 | Bark of <i>Coryaria myrtifolia</i> ..... | 13 |
| Apricot bark .....                     | 32 | Bark of <i>Rhus typhinum</i> .....       | 10 |
| Pomegranate rind .....                 | 32 | Green acorn cups .....                   | 10 |
| Oak bark .....                         | 25 | Service-tree bark .....                  | 8  |
| Cherry-tree bark .....                 | 24 | Horse chestnut bark .....                | 6  |
| Bark of the <i>Cornus mascula</i> .... | 19 | American sumach bark .....               | 6  |
| Plane-tree bark .....                  | 16 |  |    |

In the following table, the first column shows the whole quantity of extract obtained from 100 parts of the different substances, and the second column the proportion of tannine in that extract. (DAVY.)

|                         | Tannine contained in it. |      |                           | Tannine contained in it. |      |
|-------------------------|--------------------------|------|---------------------------|--------------------------|------|
| Extract.                |                          |      | Extract.                  |                          |      |
| Galls .....             | 37.5                     | 26.4 | Entire willow bark .....  | 2.2                      |      |
| Inner bark of oak ..... | 23.5                     | 16.0 | Sumach .....              | 34.3                     | 16.2 |
| — horse-chestnut ....   | 18.5                     | 15.2 | Souchong tea .....        | 32.5                     | 10.0 |
| Entire oak bark .....   | 12.7                     | 6.3  | Green tea .....           |                          | 8.5  |
| — horse chestnut do.    | 11.0                     | 4.3  | Catechu from Bombay ..... |                          | 54.3 |
| — elm bark .....        |                          | 2.7  | — — — — Bengal .....      |                          | 48.1 |

The average quantity of tannine in 480 lbs. of different barks, is as follows. (DAVY, *Agricul. Chem.*)

|                                      | lb. |                                       | lb. |
|--------------------------------------|-----|---------------------------------------|-----|
| Entire bark of middle-sized oak, cut |     | Entire bark of Lombardy poplar ....   | 15  |
| in spring .....                      | 29  | — Birch .....                         | 8   |
| — Spanish chestnut .....             | 21  | — Hazel .....                         | 14  |
| — Leicester willow, large size ....  | 33  | — Black-thorn .....                   | 16  |
| — Elm .....                          | 13  | — Coppice oak.....                    | 32  |
| — Common willow, large .....         | 11  | — Oak, cut in autumn .....            | 21  |
| — Ash .....                          | 16  | — Larch, cut in autumn .....          | 8   |
| — Beech .....                        | 10  | White interior cortical layers of oak |     |
| — Horse-chestnut .....               | 9   | bark .....                            | 72  |
| — Sycamore.....                      | 11  |                                       |     |

The following plants contain the modification of tannine which renders solutions of peroxide of iron *deep-blue*. (GMELIN.) *Galls*; the *roots* of *Lithrum salicaria*, *Geum urbanum* and *rivale*, *Potentilla argentea* and *anserina*, *Sanguisorba officinalis*, *Poterium sanguisorba*, *Alchemilla vulgaris*, *Arctium lappa*, *Polygonum bistorta*, *Iris pseudacorus*, *Nymphaea alba*; the *wood* of the oak, and many other trees; the *bark* of different species of oak; the *twigs* of the black currant and of sumach; the *leaves* of oak, *Uva ursi*, and many others; the *petals* of pomegranate, *Rosa gallica*, and *Pæonia officinalis*.

The tannine which gives a *green* precipitate with persalts of iron, is found in *catechu* and in *kino*; in the *roots* of the *Tormentilla erecta*, *Potentilla reptans*, *Rosa canina*, *Rheum rhaponticum*, &c.; in the different species of *Cinchona bark*, in *cinnamon*, *cassia*, and in *horse-chestnut bark*; in the *leaves* of *Salvia officinalis*, *Lamium album*, *Glechoma hederacea*, &c.; in the varieties of *tea*; in the *flowers* of *Tilia Europæa*, *Centaurea cyanus*, and *Arnica montana*; in *horse-chestnuts*, *date-stones*, &c.

**ARTIFICIAL TANNINE.** A substance having some of the characters of tannine, and which has therefore been called *artificial tannine*, may be formed by digesting charcoal in dilute nitric acid during several days; it is at length dissolved, and a reddish-brown liquor is obtained, which furnishes, by careful evaporation, a brown glossy substance, amounting to about 120 parts from 100 of charcoal.

This *artificial tannine* differs in one circumstance from natural tannine, which is, that it resists the action of nitric acid, by which all the varieties of natural tannine are decomposed, though some are more capable of resisting its action than others.

Artificial tannine has a bitterish astringent taste, is soluble in water and alcohol, and forms an insoluble precipitate in solutions of animal gelatine, consisting, according to Hatchett, of

|                       |
|-----------------------|
| 36 artificial tannine |
| 64 gelatine           |
| <hr/>                 |
| 100                   |

Hydrochloric and sulphuric acids occasion brown precipitates in solution of artificial tannine, which are soluble in hot water. It combines with the alkalis, and forms a precipitate of difficult solubility in aqueous solutions of lime, baryta, and strontia, and in most metallic solutions: these precipitates are of a brown color.

A variety of artificial tannine is formed by digesting camphor and resins in sulphuric acid, till the liquor becomes black, and on being



poured into water, deposits a black powder, which, by digestion in alcohol, furnishes a brown matter, soluble in water, and forming an insoluble precipitate with gelatine. (HATCHETT, *Phil. Trans.*, 1805, 1806.)

X. OXALIC ACID,  $C_2O_3 + HO$ . This acid, which was discovered by Scheele, in 1776, (THOMSON, *Inorg. Chem.*, ii. 15,) is found in some fruits, and in considerable quantity in the juice of the *Oxalis acetosella*, or *wood sorrel*, in the *Rumex acetosa*, or *common sorrel*, the varieties of *rhubarb*, and several other plants; in these it generally exists combined with potassa or lime. (BRACONNOT, *Ann. Ch. et Ph.*, xxviii. 315.) It is occasionally found in human urine; and it occurs in the mineral kingdom in combination with oxide of iron, forming the substance called *Humboldtite*.

Oxalic acid is most readily procured by the action of nitric acid on certain organic substances, and especially upon sugar, and has hence been termed *acid of sugar*. (1.) It may be obtained by introducing into a retort 4 ounces of nitric acid diluted with 2 of water, and 1 ounce of white sugar; nitric oxide gas is copiously evolved, and when the sugar is dissolved, about one-third of the acid may be distilled over: the contents of the retort are then emptied into a shallow vessel, and in the course of two or three days an abundant crop of white crystals is deposited, and, upon further evaporation of the mother liquor, a second portion is obtained. The whole crystalline produce is to be redissolved in water, and again crystallized, by which the pure acid is obtained. In this way sugar yields about half its weight of oxalic acid. (2.) Potato starch may be substituted for sugar in this process, 12 parts of which yield about 5 of the acid. Robiquet directs 24 parts of starch to be heated with 72 of nitric acid, and when the action has ceased to add 24 parts more of acid, and set the liquor aside for crystallisation, when about 5 parts of oxalic acid are obtained: 24 parts of acid are then added to the mother liquor, in divided portions, and by repeated crystallisations 2 parts more of oxalic acid are procured; and this operation may be twice repeated; so that ultimately, from 24 parts of starch and 144 of nitric acid, about 12 parts of oxalic acid are obtained. (DUMAS, *Chim. App. aux Arts*, v. 118.) (3.) Oxalic acid may also be obtained by decomposing the *binoxalate of potassa* by means of acetate of lead, or of sulphuret of barium; in either case, the precipitate is washed and decomposed, whilst still moist, by dilute sulphuric acid, and the filtered liquor evaporated till it crystallises. To decompose the precipitate, 5 parts of oil of vitriol diluted with 10 of water should be used for each 5 parts of binoxalate employed. (4.) Oxalic acid may be formed by heating sugar with a solution of permanganate of potassa; it affords oxalate of potassa, peroxide of manganese, and water; 1 atom of sugar, and 6 of permanganate of potassa, yielding 6 of neutral oxalate of potassa, 10 of water, and 12 of peroxide of manganese, as in the following equation:  $C_{12}H_{10}O_{10} + 6(KO, Mn_2O_7) = 6(KO, C_2O_3) + 10HO + 12MnO_2$ . (5.) Schlesinger gives the following directions for obtaining the common crystallised, and the monohydrated acid. Dissolve 1 part of pure sugar in  $8\frac{1}{4}$  parts of nitric acid, sp. gr. 1.38, in a long-necked flask, and apply heat till the evolution of nitrous gas and carbonic acid ceases; then pour the liquid into a porcelain basin, and evaporate in a water-bath down to one-sixth of its original volume, and set aside to crystallise for 12 hours; pour



off the mother-liquor, evaporate it in a water-bath till nitric acid is no longer evolved, add to the residue a little boiling water, and set aside to crystallise. The quantity of crystals of impure oxalic acid will amount to from 50 to 60 parts, from 100 of sugar: then place them in a warm situation, so that they may effloresce, and leave them there till the odor of nitric acid is no longer perceptible, after which redissolve in water, and again crystallise. In this way, crystals of the pure terhydrated or common acid  $= \text{C}_2\text{O}_3 + 3\text{HO}$  are obtained; to convert it into the monohydrated acid,  $\text{C}_2\text{O}_3, \text{HO}$ , suffer it to effloresce at a temperature of  $212^\circ$ , till it no longer loses weight; then put it into a matrass immersed into an oil-bath, so that the oil may stand a little above the level of the acid within, and heat up to between  $300^\circ$  and  $320^\circ$ , when the acid slowly sublimes without any decomposition, which only ensues when the temperature rises above  $320^\circ$ ; the fixed residue usually consists of a little oxalate of potassa and oxalate of lime. The matrass is then taken out of the oil bath, suffered to cool, wiped clean, and the bottom is cut off so that the sublimed acid may be removed without falling back upon the residue; it is now chemically pure monohydrated oxalic acid. (BERZELIUS, *Lehrbuch*, i. 626.)

The ordinary crystals of oxalic acid ( $\text{C}_2\text{O}_3, \text{HO} + 2\text{HO}$ ) are transparent four-sided prisms; their primary form is a right rhombic prism, the modifications of which have been described by Brooke. (*Ann. of Phil.*, N.S., vi. 119.) They are intensely sour, and dissolve in about 15 parts of water at  $50^\circ$  and in 9 parts at  $60^\circ$ , their solubility increasing rapidly with the increase of temperature; at  $212^\circ$ , they fuse in their water of crystallisation. According to Turner, 100 parts of water at  $50^\circ$  dissolve 6.9 of the crystals of oxalic acid; at  $52^\circ$  10.5 parts; and at  $60^\circ$  11.5 parts, the sp. gr. of the solution being then 1.045. At  $212^\circ$  any quantity is dissolved, and the solution concretes on cooling. The great solubility attributed to this acid by Bergman, seems to have depended upon the presence of nitric acid. It is less soluble in alcohol than in water, and still less soluble in ether. In a very dry air the crystals effloresce; at a temperature of  $100^\circ$ , they gradually fall into a white powder, and when thus slowly dried lose about a third of their weight, but as the acid is volatile, its desiccation requires caution; the crystals, after having been deprived of 2 equivalents of water, sublime, as above stated, when heated to about  $320^\circ$ ; and the sublimate contains 1 atom of water. When the ordinary crystals are rapidly heated in a retort to about  $350^\circ$ , water, carbonic acid, carbonic oxide, and formic acid, are the results. Passed through a red-hot tube, oxalic acid yields carbonic oxide and acid, and carburetted hydrogen; and a little charcoal, with a trace of oily matter, is deposited.

The sublimed *monohydrated* acid, when heated to about  $275^\circ$ , begins to volatilize, without fusion; it rises most rapidly between  $300^\circ$  and  $320^\circ$ ; at  $340^\circ$  it begins to be decomposed, becoming yellow, and evolving carbonic acid, water, and formic acid. At  $420^\circ$  the acid boils, and at  $430^\circ$  large crystals sublime, which at  $450^\circ$  are resolved without residue into gaseous products. (SCHLESINGER.) Berzelius observes that the last-mentioned crystals are perhaps anhydrous oxalic acid; they have not been examined, but it is stated that at the temperature at which they are formed, namely,  $340^\circ$ , the atom of water belonging to the acid, is suddenly given off.



Hydrochloric acid dissolves oxalic acid without decomposition. It is not decomposed by dilute nitric acid, but, when heated with concentrated nitric acid, it is converted by oxidizement into carbonic acid. Mixed with about 20 parts of sulphuric acid, and gently heated, it is rapidly resolved into equal volumes of carbonic acid and carbonic oxide, which gases are evolved, whilst the water of the crystals remains combined with the sulphuric acid (p. 450). Oxalic acid absorbs chlorine, and the resulting compound is resolved by the action of water into hydrochloric and carbonic acids. (*Ann. Ch. et Ph.*, xix. 84.) The intensity of the acidity of oxalic acid is such, that 1 part in 200,000 of water reddens litmus. It abstracts lime from sulphuric acid when added to a solution of sulphate of lime, but oxalate of lead is decomposed by sulphuric acid; so that its affinity for bases appears to be about equal to that of sulphuric acid. When a solution of oxalic acid is boiled with the peroxides of manganese, lead, cobalt, or nickel, or with chromic acid, those oxides are partially reduced, carbonic acid is evolved, and oxalates are formed. Oxalic acid boiled with chloride of gold throws down metallic gold, and carbonic acid passes off. Pure oxalic acid has no action upon paper. It is extremely poisonous, and many accidents have occurred from its resemblance in external appearance to Epsom salt (sulphate of magnesia), and from the carelessness with which medicines are often dispensed and taken. The intense sourness of oxalic acid, and the saline bitterness of the sulphate, readily distinguish them; chalk or whiting, or magnesia or carbonate of magnesia, or large draughts of soap and water, are the most ready antidotes. Oxalic acid should be perfectly volatile, and its solution not be discolored by sulphuretted hydrogen. It is sometimes contaminated by tartaric acid, and by sulphate of potassa: if it contain tartaric acid it is blackened when digested in sulphuric acid: the presence of sulphate of potassa is indicated by the insolubility in nitric acid of the precipitate occasioned in its solution by chloride of barium.

The composition of oxalic acid is a subject which has engaged much attention, since Döbereiner first suggested the non-existence of hydrogen as one of its ultimate elements, and showed that in its *anhydrous* state, as it exists in combination with certain bases, as, for instance, with oxide of lead, it might be regarded as a binary compound of carbon and oxygen = C<sub>2</sub> O<sub>3</sub>, or CO, CO<sub>2</sub>. Its equivalent, founded upon this view, is 36, and it consists of

|                       |   |     |    |     |        |    |                |   |     |    |     |       |
|-----------------------|---|-----|----|-----|--------|----|----------------|---|-----|----|-----|-------|
| Carbon .....          | 2 | ... | 12 | ... | 33.33  | or | Carbonic oxide | 1 | ... | 14 | ... | 38.9  |
| Oxygen .....          | 3 | ... | 24 | ... | 66.67  |    | Carbonic acid  | 1 | ... | 22 | ... | 61.1  |
| <hr/>                 |   |     |    |     |        |    |                |   |     |    |     |       |
| Anhydrous oxalic acid | 1 |     | 36 |     | 100.00 |    |                | 1 |     | 36 |     | 100.0 |

The *ordinary crystals* contain 3HO, or

|                              |   |     |    |     |        | Berzelius. | Prout. |
|------------------------------|---|-----|----|-----|--------|------------|--------|
| Anhydrous oxalic acid ....   | 1 | ... | 36 | ... | 57.14  | ...        | 57.15  |
| Water .....                  | 3 | ... | 27 | ... | 42.86  | ...        | 42.85  |
| <hr/>                        |   |     |    |     |        |            |        |
| Crystallized oxalic acid.... | 1 |     | 63 |     | 100.00 | 100        | 100.00 |

And the crystals, dried as far as possible without decomposition, lose 2 atoms, or about 28 *per cent.* of water, becoming C<sub>2</sub> O<sub>3</sub>, HO.

|                                |   |     |    |     |     | Berzelius. |
|--------------------------------|---|-----|----|-----|-----|------------|
| Anhydrous oxalic acid .....    | 1 | ... | 36 | ... | 80  | 80.5       |
| Water .....                    | 1 | ... | 9  | ... | 20  | 19.5       |
| <hr/>                          |   |     |    |     |     |            |
| Monohydrated oxalic acid ..... | 1 |     | 45 |     | 100 | 100.0      |

The intense acidity of oxalic, as opposed to carbonic acid, led Dulong to consider it as a *hydracid* formed of carbonic acid and hydrogen, the true oxalic or hydrocarbonic acid being, according to him, the preceding monohydrated acid, the elements of which are  $= C_2 O_4 H$ , or  $2 [CO_2] + H$ . If the radical of oxalic acid be regarded as  $C_2 O_2$  (*oxalyle*), then the formula of the anhydrous acid will be  $[C_2 O_2] O$ , and that of the monohydrated acid  $[C_2 O_2] O + HO$ .

*Oxalates*.—In the neutral oxalates the oxygen of the base is to that of the acid is 1 : 3, their formula being  $MO, C_2 O_3$ ; and if the oxygen of the base be added to the acid, the result is a metal and carbonic acid, or  $M, 2 [CO_2]$ . Many of the oxalates, when heated, give this result: thus oxalate of silver yields, when heated, metallic silver and carbonic acid;  $AgO, C_2 O_3 = Ag + 2 [CO_2]$ . Sometimes carbonic oxide and carbonic acid are given off, leaving a protoxide of the metal; this is the case with oxalate of manganese;  $MnO, C_2 O_3 = MnO, + CO, + CO_2$ ; and sometimes the carbonic oxide thus evolved reacts on the metallic oxide, and reduces it; thus with oxalate of cobalt,  $CoO, C_2 O_3 = CoO + CO + CO_2$ ; and  $CoO, + CO = Co + CO_2$ . When the oxalates are heated with sulphuric acid, they are decomposed, and yield carbonic oxide and carbonic acid, without any separation of carbon. In the acid oxalates the quantity of acid is either twice, or four times, that contained in the neutral oxalates.

*Oxalate of Ammonia*.  $NH_4 O, C_2 O_3, + HO$ . This curious salt is generally obtained by saturating a hot solution of oxalic acid by carbonate of ammonia, and crystallizing. It forms prismatic crystals, (BROOKE, *Ann. of Phil.*, N.S., vi. 374,) of which 45 parts require 1000 of cold water for their solution, but they are much more soluble in hot water, (soluble in 28 parts of cold water, BERZELIUS.) They are insoluble in alcohol. Added to any soluble compound of lime, this salt produces an insoluble *oxalate of lime*, provided no excess of acid be present; hence its use as a test of the presence of lime in water. The crystals of oxalate of ammonia contain 2 atoms of water, 1 of which may be expelled by heat, when they crumble into a white powder. Their composition is

|                                       |   |      |    |      |        |
|---------------------------------------|---|------|----|------|--------|
| Ammonia .....                         | 1 | .... | 17 | .... | 23.95  |
| Oxalic acid .....                     | 1 | .... | 36 | .... | 50.70  |
| Water .....                           | 2 | .... | 18 | .... | 25.35  |
| <hr/>                                 |   |      |    |      |        |
| Crystallized oxalate of ammonia ..... | 1 |      | 71 |      | 100.00 |

The effloresced, or dry oxalate of ammonia, contains

|                                |   |      |    |      | Berzelius. | Berard. | Thomson. |       |        |      |        |
|--------------------------------|---|------|----|------|------------|---------|----------|-------|--------|------|--------|
| Ammonia .....                  | 1 | .... | 17 | .... | 27.42      | ....    | 26.88    | ....  | 27.66  | .... | 25.55  |
| Oxalic acid.....               | 1 | .... | 36 | .... | 58.06      | ....    | 59.37    | }.... | 72.34  | .... | 74.45  |
| Water.....                     | 1 | .... | 9  | .... | 14.52      | ....    | 13.75    |       |        |      |        |
| <hr/>                          |   |      |    |      |            |         |          |       |        |      |        |
| Effloresced oxalate of ammonia | 1 |      | 62 |      | 100.00     |         | 100.00   |       | 100.00 |      | 100.00 |

*Binoxalate of Ammonia*,  $NH_4 O, 2C_2 O_3, 3HO$ , is less soluble than the oxalate, and may be precipitated in crystalline powder on adding an equivalent of oxalic acid to the neutral salt. It contains 3 atoms of water, one of which is basic to the oxalic acid, and cannot be expelled without the salt suffering decomposition, the formula of the salt being  $NH_4 O, C_2 O_3, + HO, C_2 O_3 + 2 HO$ . (GRAHAM.)



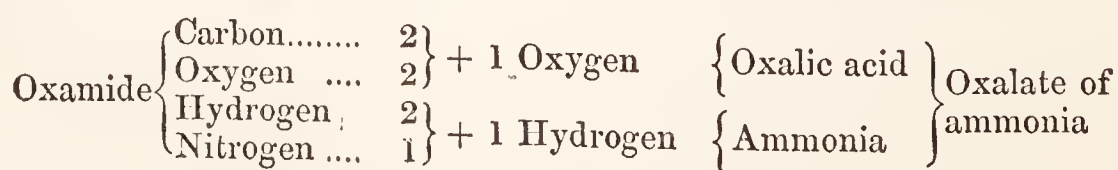
*Quadroxalate of Ammonia*,  $\text{NH}_4\text{O}$ ,  $4\text{C}_2\text{O}_3$ ,  $7\text{HO}$ , is obtained by dissolving the binoxalate together with 2 atoms of oxalic acid, in boiling water; on cooling, it affords crystals isomorphous with the corresponding potassa salt. (GRAHAM.)

**OXAMIDE, or OXALAMIDE. OXAMIC ACID.** When oxalate of ammonia is subjected to dry distillation, it first becomes opaque from loss of water, then fuses, boils, decomposes, and volatilizes, leaving a little carbon behind; the liquid which passes over contains a flocculent substance, which also lines the neck of the retort, and to which Dumas gave the name of *oxamide*; it may be separated by washing and filtration, 100 parts of the oxalate yielding about 5. The other products of the decomposition are ammonia, water, carbonic acid, carbonic oxide, and cyanogen. According to Mohr, a larger quantity of oxamide is obtained, when the oxalate is previously mixed with sal ammoniac, the vapor of which carries over the oxamide; the sal ammoniac may afterwards be washed out of the products. Oxamide is also formed by the action of ammonia on oxalic ether. (See *Ethers*.)

Oxamide forms imperfect crystallized plates, or a granulated powder, without taste or smell, and having no action on test-papers. It is volatile when carefully heated, but generally sublimes with more or less decomposition, yielding cyanogen and carbon: it is scarcely soluble in water at  $60^\circ$ , and a saturated solution at  $212^\circ$  deposits it in crystalline flocculi. It is insoluble in alcohol. It is composed of

|                |   |     |    |     | Dumas. |
|----------------|---|-----|----|-----|--------|
| Carbon .....   | 2 | ... | 12 | ... | 7.4    |
| Oxygen .....   | 2 | ... | 16 | ... | 36.3   |
| Hydrogen ..... | 2 | ... | 2  | ... | 4.5    |
| Nitrogen ..... | 1 | ... | 14 | ... | 31.8   |
| <hr/>          |   |     |    |     |        |
| Oxamide .....  | 1 |     | 44 |     | 100.0  |

Consequently oxamide differs from oxalate of ammonia in containing less water, by 2 atoms; for the elements of 44 parts of oxamide + 18 of water, = 62 oxalate of ammonia; and oxamide may, under certain circumstances, resume this elementary water, as by the action of acids or hydrated alkalis aided by heat. Boiled with potassa, or soda, oxamide evolves ammonia, and the carbon and oxygen remain in the state of oxalic acid: the dilute sulphuric, nitric, and hydrochloric acids convert it into oxalic acid, and form ammoniacal salts. Boiled with concentrated sulphuric acid, oxamide affords sulphate of ammonia, and equal volumes of carbonic acid and carbonic oxide are disengaged: concentrated nitric acid converts oxamide into nitrate of ammonia and carbonic acid. (See Malaguti, on the *Amides*, in reference to these decompositions. *Comptes Rendus*, xxii. 851, and *Chem. Gaz.*, February, 1847.) In these cases, oxamide, by decomposing an atom of water, furnishes oxalic acid and ammonia; or



The elements of oxamide, as will be seen by the above diagrams, are such as to represent 2 atoms of carbonic oxide + a compound of 2 atoms

of hydrogen and 1 of nitrogen; now it has been ingeniously suggested by Dumas that an analogy subsists between this bihydruret of nitrogen, and the bicarburet of nitrogen or cyanogen, and that both resemble the haloid bases; that is, considering  $\text{NH}_2$ , or *amidogen*, (see p. 358), as a compound analogous to cyanogen, oxamide would be a compound analogous to the cyanides and chlorides. We shall afterwards have occasion to revert to this analogy; in the mean time, it may be observed that the elements of oxamide are such as to admit of other hypothetical distributions; that they are, for instance, equivalent to nitric oxide and olefiant gas,  $\text{NO}_2$ ,  $\text{C}_2 \text{H}_2$ ; or to cyanogen and water,  $\text{NC}_2$ ,  $2\text{HO}$ . Compounds of the base,  $\text{NH}_2$ , with other substances, are also distinguished by the termination *amide*, as *potassiamide* (p. 58), *benzamide*, *succinamide*, &c.

*Oxamic acid.*  $\text{C}_2 \text{H}_4 \text{O}_5 \text{N} + \text{HO}$ . Balard has given this name to a product which he discovered among the results of the destructive distillation of binoxalate of ammonia, and which may also be obtained from the oxalate, by proper management of the heat used in its decomposition. Oxamic acid is obtained when binoxalate of ammonia is heated up to the temperature at which oxamide is formed; that salt consists of 1 atom of oxalate of oxide of ammonium and 1 atom of hydrate of oxalic acid; and the oxamide, at the moment of its production, combines with the hydrated oxalic acid to form *hydrated oxamic acid*. Balard gives the following directions for obtaining it. Heat binoxalate of ammonia in a proper vessel, in an oil bath, to between  $430^\circ$  and  $445^\circ$ , stirring it till the mass is in equal fusion, and then retain it at the same temperature till it assumes a *yellow* color. If this be done in a retort, it will be found that certain products of decomposition are evolved, namely, carbonic acid and some carbonic oxide; that water holding formic acid in solution passes over, and that a little oxamide sublimes. If the temperature be raised too high, the oxamic acid, which is not volatile, is itself decomposed, evolving carbonate of ammonia and cyanide of ammonium, and leaving a red or brown substance of a bitter taste. The above-mentioned *yellow* product is to be dissolved in cold water, and filtered from the yellow residue. The filtered liquor is then evaporated in vacuo over sulphuric acid, during which, pulverulent oxamic acid separates; but the evaporation must not be carried to dryness, inasmuch as the mother-liquor may contain oxalic acid; the oxamic acid, therefore, which falls, should be removed and dried on filtering paper. The mother-liquor may then be saturated with ammonia, and precipitated by chloride of barium, which throws down a mixture of oxalate and oxamate of baryta; this mixed precipitate is washed first with cold and then with boiling water upon a filter, when the oxamate passes through in hot solution, and the oxalate remains insoluble. If the solution be yellow, it may be boiled with animal charcoal, when white oxamate of baryta will be deposited as the filtered liquor cools, and may be decomposed by the due addition of dilute sulphuric acid. Impure oxamic acid may be purified by saturating it with ammonia, destroying the color of the solution by animal coal, and then adding a little dilute sulphuric acid, which throws down pulverulent oxamic acid.

Oxamic acid is a white sour powder; it is not volatile, but is converted, at  $246^\circ$ , into the yellow substance above adverted to, which, at a higher temperature, is itself decomposed, but which has not been further



examined. This acid is difficultly soluble in cold water, and when its solution is boiled, the oxamide contained in it is reconverted into oxalate of ammonia, so that after long boiling, the oxamic acid disappears, and is replaced by binoxalate of ammonia: hence the necessity of avoiding heat in evaporating the solution of oxamic acid. It is soluble in absolute alcohol, and this solution, when evaporated, leaves the acid in a coarser granular form, than when it is deposited from its aqueous solution. The pulverulent or granular oxamic acid is *hydrated*, and contains 1 atom of water. (BERZELIUS, *Lehrbuch*, i. 637.) The *anhydrous acid*, as it exists in combination, consists of

|                             |   |     |    |     | Balard. |     |        |     |                 |     |     |     |     |     |     |
|-----------------------------|---|-----|----|-----|---------|-----|--------|-----|-----------------|-----|-----|-----|-----|-----|-----|
| Carbon .....                | 4 | ... | 24 | ... | 30.0    | ... | 29.97  | } = | Oxamide....     | ... | 1   | ... | 44  | ... | 55  |
| Hydrogen .....              | 2 | ... | 2  | ... | 2.5     | ... | 2.49   |     | Oxalic acid.... | 1   | ... | 36  | ... | 45  |     |
| Oxygen .....                | 5 | ... | 40 | ... | 50.0    | ... | 49.88  |     |                 |     |     |     |     |     |     |
| Nitrogen .....              | 1 | ... | 14 | ... | 17.5    | ... | 17.66  |     |                 |     |     |     |     |     |     |
| <hr/>                       |   |     |    |     |         |     |        |     |                 |     |     |     |     |     |     |
| Anhydrous oxamic acid ..... | 1 |     | 80 |     | 100.0   |     | 100.00 |     |                 |     | 1   |     | 80  |     | 100 |

ture below that which occasions charring: in this way *oxalate of potassa* is produced, and is converted, at a higher temperature, into carbonate of potassa.

*Binoxalate of Potassa.*  $\text{KO}, \text{HO}, 2\text{C}_2\text{O}_3, 2\text{HO}$ . This salt may be formed by dissolving 15·8 parts of crystallized oxalic acid in 6 parts of boiling water, and adding to the hot liquor 8·6 parts of carbonate of potassa previously dissolved in a little water. The binoxalate crystallizes on cooling in small flat rhombic prisms. They include, according to Graham, 3 atoms = 18·42 *per cent.* of water, 2 of which may be expelled by heat, but 1 atom of water is retained till the salt begins to be decomposed. It has a very sour and slightly bitter taste, and when thrown upon glowing coals, exhales acid fumes, but is not carbonized. It is soluble in 40 of cold and 6 of boiling water, and is very sparingly soluble in common alcohol. This salt exists ready formed in the juice of the *Oxalis acetosella* and *corniculata*, and is known under the name of *salt of wood sorrel*. It is also found in *Rumex acetosa*, and *acetosella*, *Geranium acetosum*, &c. It is prepared from the juice of the wood-sorrel in some parts of Germany and Switzerland: it is said to be poisonous, and to have proved fatal in a case in which it was substituted for bitartrate of potassa. It is used to remove ink-stains and iron-moulds from linen.

*Quadroxalate of Potassa.*  $\text{KO}, 4\text{C}_2\text{O}_3, 7\text{HO}$ . When binoxalate of potassa is digested in nitric or hydrochloric acid, half the potassa is abstracted, and a *quadroxalate* remains. The crystals of this salt, which are oblique truncated octohedrons, include 7 atoms of water = 24·7 *per cent.* Graham represents this salt as a compound of 1 atom of binoxalate of potassa with 2 atoms of terhydrated oxalic acid,  $\text{KO}, 2\text{C}_2\text{O}_3 + \text{HO}, \text{C}_2\text{O}_3, + 2 [\text{HO}, \text{C}_2\text{O}_3, + 2\text{HO}]$  the 4 atoms of water of crystallization of the last-mentioned constituent escaping when the salt is heated to  $262^\circ$ . (*Phil. Trans.*, 1837, p. 50.) The composition of these several oxalates of potassa was originally pointed out by Wollaston, and deserves to be recorded as the first well-authenticated illustration of the theory of multiple proportionals. (*Phil. Trans.*, 1808.)

*Ammonio-oxalate of Potassa.* When the binoxalate of potassa is neutralized by an atom of ammonia, a double salt, which forms long, permanent, acicular crystals, is obtained. (BERZELIUS.)

*Oxalate of Soda*,  $\text{NaO}, \text{C}_2\text{O}_3$ , is sparingly soluble in water, and separates from its solution in small crystalline grains, which, according to Graham, are *anhydrous*; but Berard and Thomson represent them as containing 1 atom of water. The salt is formed by carefully saturating the acid with the base, but if the solution be concentrated, the salt precipitates.

*Binoxalate of Soda*,  $\text{NaO}, \text{HO}, \text{C}_2\text{O}_3, 2\text{HO}$ , gradually falls in small crystalline grains from a mixed solution of 1 atom of carbonate of soda with 2 atoms of oxalic acid. This salt scarcely loses weight when dried at  $212^\circ$ , but at  $300^\circ$  it loses 2 atoms of water, or about 14 *per cent.*; it retains the third atom of water, which is *basic*, at a higher temperature. There is no *quadroxalate of soda*. (GRAHAM.)

*Oxalate of Potassa and Soda.* This double salt forms crystals resembling alum, which effloresce in the air. (DUMAS.)

*Oxalate of Lithia* is difficultly crystallizable, and very soluble. The



*binoxalate* forms small transparent granular crystals, not so soluble as the neutral salt.

*Oxalate of Lime.* This compound exists in many plants, and is found in such quantities in some lichens, especially *Variolaria communis*, *Isidium corallinum*, *Psora candida*, &c., that the soil upon the spots on which they have grown and decayed, and trunks of old trees upon which they have flourished, abound in it; thus from the decayed wood of an old beech tree Braconnot easily obtained several ounces of this oxalate, and he has suggested these vegetables as economical sources of oxalic acid, observing that it most abounds in the crustaceous species, and diminishes as they become foliaceous. He boils the dried and pulverized lichen with its weight of crystallized carbonate of soda in a sufficient quantity of water, saturates the filtered liquor with nitric acid, and then adds acetate of lead, which gives a copious precipitate of oxalate of lead, which he decomposes by dilute sulphuric acid; sulphate of lead is formed, and the filtered liquor yields crystals of oxalic acid on evaporation. In other cases he decomposes the pulverized *variolaria* at once by oil of vitriol, then adds water, filters, and evaporates, by which a crop of crystals of oxalic acid is obtained. (*Ann. Ch. et Ph.*, xxviii. 320.) The little transparent bodies called *raphides*, found in the cellular tissue, and floating occasionally in the juices of vegetables, as in the sap of very old trees, and in the juice of the common hyacinth, are composed, according to Raspail, of oxalate of lime; this salt also exists occasionally in the human urine, and forms calculi, which, from their rough or nodular exterior and brown color, are generally called *Mulberry calculi*. On adding oxalic acid or oxalate of ammonia to any solution of lime, oxalate of lime is precipitated: it is insoluble in water, and in excess of oxalic acid, but dissolves in hydrochloric and nitric acids: hence in testing *acid solutions* for lime, by oxalic acid, or oxalate of ammonia, the excess of acid should be previously neutralized. When oxalate of lime is digested in a solution of a carbonated alkali, carbonate of lime and an alkaline oxalate are formed. It is sometimes stated that, in consequence of the high affinity between oxalic acid and lime, and the insolubility of the oxalate, that salt cannot be decomposed by other acids or bases: it is, however, decomposed by sulphuric acid when too much water is not present, although oxalic acid throws down oxalate of lime from an aqueous solution of sulphate of lime. When rendered dry upon a sand-heat, this salt becomes singularly electrical on friction, as when stirred about with a glass or metal rod. Glass, and platinum and other metals rubbed against the powder, become negative, the powder positive; it appears to stand at the head of the list of substances, as to its power of becoming positive by friction. (FARADAY.) It retains its electric power when cold, but gradually loses it on exposure to the air, in consequence of the absorption of moisture. At a red heat it is converted first into carbonate, and then into quicklime. When recently precipitated, well washed, and dried by mere exposure to air, it consists of

|                    |   |     |    |     |       |     | Thomson. |
|--------------------|---|-----|----|-----|-------|-----|----------|
| Lime .....         | 1 | ... | 28 | ... | 34.1  | ... | 33.98    |
| Oxalic acid .....  | 1 | ... | 36 | ... | 43.9  | ... | 43.69    |
| Water .....        | 2 | ... | 18 | ... | 22.0  | ... | 22.33    |
| <hr/>              |   |     |    |     |       |     |          |
| Dried at 60° ..... | 1 |     | 82 |     | 100.0 |     | 100.00   |

When kept at  $212^{\circ}$ , till it no longer loses weight, it appears to consist of

|               |   |     |       |     |       | Vogel. | Berard. | Gay Lussao<br>and Thenard. |
|---------------|---|-----|-------|-----|-------|--------|---------|----------------------------|
| Lime .....    | 1 | ... | 28    | ... | 38.4  | ...    | 38.5    | ...                        |
| Oxalic acid   | 1 | ... | 36    | ... | 49.3  | ...    | 49.5    | ...                        |
| Water .....   | 1 | ... | 9     | ... | 12.3  | ...    | 12.0    | ...                        |
| <hr/>         |   |     | <hr/> |     | <hr/> |        | <hr/>   |                            |
| Dried at 212° | 1 |     | 73    |     | 100.0 |        | 100.0   |                            |
|               |   |     |       |     |       |        | 100     | 100.000                    |

When dried at  $500^{\circ}$ , it becomes *anhydrous*, and then contains

|                     |   |     |    |     |       | Vogel.<br>Thomson. | Dumas. |     |        |
|---------------------|---|-----|----|-----|-------|--------------------|--------|-----|--------|
| Lime .....          | 1 | ... | 28 | ... | 43·7  | ...                | 43·75  | ... | 44·01  |
| Oxalic acid .....   | 1 | ... | 36 | ... | 56·3  | ...                | 56·25  | ... | 55·99  |
| <hr/>               |   |     |    |     |       |                    |        |     |        |
| Dried at 500° ..... | 1 |     | 64 |     | 100·0 |                    | 100·00 |     | 100·00 |

As oxalate of lime is frequently referred to in quantitative analysis, the degree of desiccation must be, in such cases, attentively observed; and it must also be recollected that it is hygrometric. But it is, perhaps, better to convert it by heat and sulphuric acid into *anhydrous sulphate of lime*, the equivalent of which is more certain. According to Graham, (*Phil. Trans.*, 1837, p. 49,) oxalate of lime forms only one definite hydrate, containing 2 atoms of water, and parts with the whole of its constitutional water at a moderate temperature.

A compound of *chloride of calcium with oxalate of lime*, containing water of crystallization, is obtained in good crystals, which are persistent in the air, by dissolving oxalate of lime to saturation in hot hydrochloric acid, and allowing the solution to cool; it consists of 1 equivalent of each salt, with 7 equivalents of water. (FRITZCHE.) Oxalate of lime is known to combine with 2 equivalents of water, of which 1 appears to remain in this double salt, while the other is replaced by chloride of calcium, carrying its 6 atoms of water of crystallization along with it. (GRAHAM.)

*Oxalate of Baryta* is very nearly insoluble. It cannot be obtained in an anhydrous state, but when dried at  $212^{\circ}$ , contains

|                   |   |     |     |     |       | Berard. | Graham. |     |        |
|-------------------|---|-----|-----|-----|-------|---------|---------|-----|--------|
| Baryta .....      | 1 | ... | 77  | ... | 63·1  | ...     | 62·17   | ... | 62·85  |
| Oxalic acid.....  | 1 | ... | 36  | ... | 29·5  | }       | 37·83   | ... | 37·15  |
| Water .....       | 1 | ... | 9   | ... | 7·4   |         |         |     |        |
| <hr/>             |   |     |     |     |       |         |         |     |        |
| Oxalate of baryta | 1 |     | 122 |     | 100·0 |         | 100·00  |     | 100·00 |

*Binoxalate of Baryta* is formed by boiling excess of oxalic acid with carbonate or nitrate of baryta; on cooling it is deposited in transparent crystals. Boiling water resolves these into a precipitate of neutral oxalate and free acid. The crystals contain

|                           |   |     |       |     |       |         |       |
|---------------------------|---|-----|-------|-----|-------|---------|-------|
|                           |   |     |       |     |       | Berard. |       |
| Baryta .....              | 1 | ... | 77    | ... | 46.1  | ...     | 45    |
| Oxalic acid .....         | 2 | ... | 72    | ... | 43.1  | }       | ...   |
| Water .....               | 2 | ... | 18    | ... | 10.8  |         |       |
| <hr/>                     |   |     | <hr/> |     | <hr/> |         | <hr/> |
| Binoxalate of baryta .... | 1 |     | 167   |     | 100.0 |         | 100   |

According to Thomson, this salt consists of 2 atoms of oxalic acid, 1 of baryta, and 3 of water. (*Inorg. Chem.*, Ed. 1831, 486.) Graham



failed in obtaining a binoxalate of baryta, and is of opinion that no supersalt of this acid with the magnesian class of oxides exists.

*Oxalate of Strontia* is a white tasteless powder nearly insoluble in water (in 1920 boiling water, HOPE.) It contains 1 atom of oxalic acid, 1 of strontia, and 2 of water. By digesting it in an aqueous solution of oxalic acid, a *binoxalate of strontia* is formed, which may be obtained in anhydrous prismatic crystals. (THOMSON.) Graham denies the existence of this binoxalate.

*Oxalate of Magnesia* is a white, tasteless, and almost insoluble powder; it is thrown down when oxalate of potassa is added to sulphate of magnesia. Oxalate of magnesia, when dried at  $212^{\circ}$ , retains between 27 and 28 per cent. = 2 atoms, of water; even at  $300^{\circ}$  it does not part with its constituent water, but remains  $\text{MgO}, \text{C}_2\text{O}_3, 2\text{HO}$ . The crystals which are obtained on mixing together solutions of binoxalate of potassa and sulphate of magnesia, and which have been supposed to be a *binoxalate of magnesia*, (THOMSON, *First Principles*, II., 307,) are merely a mixture of oxalate of magnesia and quadroxalate of potassa: hence there is no combination of oxalate of magnesia with oxalate of water. (GRAHAM.)

*Oxalate of Ammonia and Magnesia*. This double salt is formed when concentrated solutions of chloride of magnesium and oxalate of ammonia are mixed; after some hours it is deposited in acicular crystals, or if procured by evaporation, forms saline crusts, containing, according to Wächter, 4.44 per cent. of magnesia, and 19.32 water. It requires 480 parts of water for solution, but is much more soluble if any ammoniacal salt be present, so that dissolved in dilute nitric or hydrochloric acid, and then saturated with ammonia, it is retained in solution. It is thus that we are enabled, by means of oxalate of ammonia, to separate lime from magnesia.

*Oxalate of Manganese*. Oxalic acid and oxalate of ammonia throw down a white powder from solutions of the protosalts of manganese, which acquires a red tint on drying. When dried at  $212^{\circ}$ , it is  $\text{MnO}, \text{C}_2\text{O}_3, 2\text{HO}$ . (GRAHAM.) Free oxalic acid increases its solubility in hot water. It is very sparingly soluble in caustic ammonia.

*Oxalate of Ammonia and Manganese* is formed by dissolving the preceding salt in a hot solution of oxalate of ammonia; on cooling it deposits acicular crystals. When ammonia is added to their aqueous solution, a basic ammonio-oxalate falls in the form of a crystalline precipitate. (WINCKELBLECH.)

*Oxalate of Potassa and Manganese* is formed, as the preceding salt, by dissolving the oxalate of manganese in a boiling solution of oxalate of potassa: it also forms acicular crystals.

*Oxalates of Iron*. The *protoxalate* crystallizes with excess of acid, in green prisms, and may be formed by digesting iron in a solution of oxalic acid: the neutral oxalate falls when the solution becomes saturated. The *peroxalate* is thrown down from the perchloride or persulphate of iron, by the soluble oxalates, in the form of a difficultly-soluble yellow powder, which is long in subsiding, and which is taken up again by excess of oxalic acid: hence the use of this acid in removing iron-moulds, which it does without injuring the texture of linen. The precipitated peroxalate, when dissolved in oxalic acid, may be obtained in small greenish-yellow prismatic crystals: when their solution is exposed



to the direct rays of the sun, carbonic acid is evolved, and the peroxalate is reduced to protoxalate, which forms a granular deposit. (DÖBEREINER.) Pure Prussian blue is soluble in oxalic acid, and this solution diluted with water is used as a writing fluid. When oxalic acid is present in very dilute solutions of iron, the indication of iron by ferrocyanide of potassium is prevented. (J. T. COOPER.)

*Oxalate of Ammonia and Iron* is formed by digesting hydrated peroxide of iron in solution of binoxalate of ammonia: it forms small green octohedra, soluble in 0.9 of water at 68°, and in 0.7 at 212°. (BERZELIUS.)

*Oxalate of Potassa and Iron.*  $\text{Fe}_2\text{O}_3, 3\text{C}_2\text{O}_3, + 3[\text{KO}, \text{C}_2\text{O}_3] + 6\text{HO}$ . Graham formed this salt by dissolving hydrated peroxide of iron to saturation, in binoxalate of potassa; a sap-green solution results, which, when concentrated, deposits tabular crystals of a grass-green color, which effloresce in very dry air. The peroxide of iron of this salt is completely thrown down by ammonia. It might be useful in pharmacy.

*Oxalate of Soda and Iron*, forms green crystals, which contain 10 atoms of water. (GRAHAM.)

*Oxalate of Zinc.*  $\text{ZnO}, \text{C}_2\text{O}_3, 2\text{HO}$ , is formed by adding oxalic acid to a soluble salt of zinc: it is a white powder, nearly insoluble. (SCHINDLER. GRAHAM.) Schindler has also described an *oxalate of ammonia and zinc*, and an *oxalate of potassa and zinc*. (BERZELIUS, *Lehrbuch*.)

*Oxalate of Tin* is formed, according to Bergman, by digesting the metal in excess of the acid; hydrogen is evolved, and the solution, slowly evaporated, gives prismatic crystals of an acid protoxalate of tin. The neutral salt forms an insoluble white powder.

*Oxalate of Cadmium* is a white insoluble powder.

*Oxalate of Cobalt* is an insoluble red powder, precipitated by oxalic acid from neutral solutions of cobalt. It dissolves in excess of oxalic acid, and the solution furnishes crystals. The dry salt yields, when heated in a tube, 0.3286 metallic cobalt, 0.4757 carbonic acid, and 0.1957 water; it therefore consists of 1 atom of oxide of cobalt, 1 of oxalic acid, and 2 of water. When carefully heated, it loses water, and then burns in the air. (DÖBEREINER.) It is sparingly soluble in caustic, but abundantly soluble in carbonate of ammonia. When this salt is digested in a cold solution of potassa, it becomes blue, and passes into a basic oxalate; by boiling it in solution of potassa, the whole of the acid is abstracted.

*Oxalate of Ammonia and Cobalt.* A compound of 1 atom of oxalate of cobalt combined with 9 of oxalate of ammonia is formed, according to Winckelblech, by boiling the two salts together; a red solution is obtained, which deposits the double salt in pale red crystals containing 28 *per cent.* of water. When ammonia is added to a solution of this salt, it gradually deposits a reddish-brown precipitate, insoluble in water, and only partially soluble in oxalic acid  $= 2[\text{CoO}, \text{C}_2\text{O}_3] + \text{NH}_3 + 6\text{HO}$ . (BERZELIUS.)

*Oxalate of Nickel* is thrown down from the nitrate, and from all neutral solutions of nickel, in the form of a green powder, insoluble in excess of oxalic acid. It contains 13.4 *per cent.* ( $= 2$  atoms) of water:



heated in a retort it yields carbonic acid and metallic nickel: it forms double salts with the oxalates of ammonia, potassa, and soda.

*Oxalate of Copper.* When oxalic acid is added to sulphate or nitrate of copper, *oxalate of copper* is thrown down in the form of a green powder, soluble in excess of the acid, and yielding a solution from which prismatic green crystals may be obtained.

*Oxalate of Ammonia and Copper.* This, and several other *double oxalates of copper*, have been described by Vogel. (*Schweigger's Journal*, vii.) By digesting oxalate of copper in a solution of oxalate of ammonia, and filtering, rhomboidal crystals were obtained on evaporation, which detonated when suddenly heated: when slowly heated, they merely lost water and ammonia. Graham obtained this salt by dissolving hydrated oxide of copper in binoxalate of potassa: he represents it as  $\text{CuO}, \text{C}_2 \text{O}_3, + \text{NH}_4 \text{O}, \text{C}_2 \text{O}_3, + 2\text{HO}$ . At  $212^\circ$  the crystals lose 11.5 per cent. = 2 atoms of water. The analysis of this salt gives

|                       |   |      |     |      |        | F. C. Vogel. |
|-----------------------|---|------|-----|------|--------|--------------|
| Ammonia .....         | 1 | .... | 17  | .... | 10.90  | .... 10.5    |
| Oxide of copper ..... | 1 | .... | 40  | .... | 25.64  | .... 25.0    |
| Oxalic acid .....     | 2 | .... | 72  | .... | 46.15  | .... 47.5    |
| Water .....           | 3 | .... | 27  | .... | 17.31  | .... 17.0    |
|                       |   | —    | —   | —    | —      | —            |
|                       |   | 1    | 156 |      | 100.00 | 100.0        |

By digesting oxalate of copper in caustic ammonia, and pouring the solution thus obtained into a shallow basin, it deposits flat six-sided prisms of a blue color, which effloresce on exposure to air. The undissolved portion of the oxalate also combines with ammonia, and produces another distinct compound.

*Oxalate of Potassa and Copper* is obtained by digesting carbonate of copper in solution of binoxalate of potassa. Prismatic and rhomboidal crystals are formed, which Vogel considers as two distinct salts; the former consisting of 1 equivalent of oxalate of copper, 1 of oxalate of potassa, and 4 of water; and the latter, of 1 of oxalate of copper, 1 of oxalate of potassa, and 2 of water. The former crystals become opaque by exposure to air, and lose 2 atoms of water by efflorescence.

*Oxalate of Soda and Copper.* Vogel has also described two crystalline varieties of this salt. (*Schweigger's Journal*, vii.)

*Oxalate of Lead* is thrown down in crystalline grains on adding oxalic acid to nitrate of lead. It is insoluble in water, but dissolves sparingly in excess of oxalic acid. Heated in close vessels it leaves a suboxide of lead, (p. 849): in the air it leaves oxide of lead: when heated in a tube with potassium, it detonates violently: it is anhydrous when dried at  $212^\circ$ , and consists of

|                     |   |      |     |      |        | Berzelius. |
|---------------------|---|------|-----|------|--------|------------|
| Oxide of lead ..... | 1 | .... | 112 | .... | 75.68  | .... 75.46 |
| Oxalic acid .....   | 1 | .... | 36  | .... | 24.32  | .... 24.54 |
|                     |   | —    | —   | —    | —      | —          |
|                     |   | 1    | 148 |      | 100.00 | 100.00     |

Pelouze has described a *basic oxalate of lead*, obtained by precipitating bibasic acetate of lead with neutral oxalate of ammonia, when it falls in the form of white powder. He also obtained it by boiling excess of oxamide in solution of nitrate or of acetate of lead, and filtering the

hot liquor, when it was deposited in delicate crystals. Exposed to air, the excess of oxide of lead absorbs carbonic acid.

When oxide or carbonate of lead is digested in a solution of binoxalate of potassa, an *oxalate of potassa and lead* is obtained in permanent acicular crystals.

By saturating warm nitric acid with oxalate of lead, Johnston obtained a double salt  $= \text{PbO}, \text{C}_2\text{O}_3 + \text{PbO}, \text{NO}_5 + 2\text{HO}$ , in the form of rhombic tables: it is resolved by cold water into its constituent salts. It is also formed when solutions containing nitric and oxalic acids are precipitated by acetate of lead. Pelouze has described a basic double salt,  $= 4\text{PbO}, \text{NO}_5, \text{C}_2\text{O}_3$ , obtained by adding ammonia to a hot solution of oxamide in nitrate of lead. (BERZELIUS, *Lehrbuch*.)

*Oxalate of Antimony*,  $\text{SbO}_3, 3\text{C}_2\text{O}_3$ , is obtained either by digesting the oxide in the acid, or by dropping oxalic acid into a solution of acetate of antimony. It is a difficultly soluble crystalline powder.

*Oxalate of Potassa and Antimony*, is obtained by digesting oxide of antimony in a solution of binoxalate of potassa: it forms stellated crystals, containing 20.19 *per cent.* of water, and soluble in 10 parts of water at  $50^\circ$ . (LASSAIGNE.) According to Bussy, there is a salt in rhombic prisms, consisting of  $3[\text{KO}, \text{C}_2\text{O}_3] + \text{SbO}_3, 3\text{C}_2\text{O}_3 + 6\text{HO}$ , which is soluble in a small quantity of water, but decomposed in dilute solution. (BERZELIUS, *Lehrbuch*.)

*Oxalate of Bismuth* is deposited in crystalline grains, when solution of oxalic acid is dropped into nitrate of bismuth. It is also produced in the form of a white powder, by digesting hydrated oxide of bismuth in a strong aqueous solution of oxalic acid: it is decomposed by water, and leaves a basic salt when washed with boiling water.

*Oxalate of Uranium*. The *protoxalate* is very sparingly soluble in hot or cold water; it may be obtained by mixing solutions of the protochloride and oxalic acid, and washing the precipitate in boiling water to free it from any peroxalate: it is white, with a slight shade of green, and not affected by air: it contains, when dried in the air, 3 equivalents of water, but of these it loses 2 when dried in vacuo: its composition in the former case is

|                             |   |     |     |     |       | Peligot. |
|-----------------------------|---|-----|-----|-----|-------|----------|
| Protoxide of uranium .....  | 1 | ... | 68  | ... | 52.3  | 51.2     |
| Oxalic acid .....           | 1 | ... | 36  | ... | 27.3  | 28.5     |
| Water .....                 | 3 | ... | 27  | ... | 20.4  | 20.3     |
| <hr/>                       |   |     |     |     |       |          |
| Protoxalate of uranium .... | 1 |     | 131 |     | 100.0 | 100.0    |

The *peroxalate of Uranium*, (*Oxalate of Uranyle* of Peligot, *Ann. Ch. et Ph.*, 3me Ser. 1842, v. 40,) falls in the form of a yellow granular crystalline powder, when concentrated solutions of oxalic acid and pernitrate of uranium are mixed: it is very sparingly soluble in cold water, and is deposited in small granular crystals from its hot solution, so that it is easily washed by decantation: it consists of

|                                    |   |     |     |     |       | Peligot. |
|------------------------------------|---|-----|-----|-----|-------|----------|
| Peroxide of uranium .....          | 1 | ... | 144 | ... | 69.3  | 69.5     |
| Oxalic acid .....                  | 1 | ... | 36  | ... | 17.3  | 17.5     |
| Water .....                        | 3 | ... | 27  | ... | 12.9  | 13.0     |
| <hr/>                              |   |     |     |     |       |          |
| Crystallized peroxalate of uranium | 1 |     | 207 |     | 100.0 | 100.0    |



The peroxalate of uranium is soluble to a considerable extent in a hot solution of oxalate of ammonia, and yields a double salt, in yellow transparent prisms, containing an atom of each of the oxalates and 4 of water; or, as represented by Peligot, as follows:— $[U_2 O_2] O, C_2 O_3 + NH_4 O, C_2 O_3 + 3HO$ .

*Oxalate of Cerium* is precipitated by the addition of oxalic acid or oxalate of ammonia to solutions of the protoxide of cerium, of a white color, insoluble in excess of acid, but soluble in liquid ammonia. In solutions of the peroxide of cerium, the precipitate is red, and soluble in ammonia.

*Oxalate of Chromium*,  $Cr_2 O_3, 3C_2 O_3$ , is obtained by dissolving the hydrated oxide in the acid; the solution is cherry-red, becoming green when heated, and leaving a green mass on evaporation: it forms no crystallizable compound with excess of oxalic acid, the free acid crystallizing only when evaporated. The solution of this oxalate is not precipitated by caustic ammonia, nor by the salts of lime, but by lime water, and by caustic potassa when heated. Oxalate of chromium forms a variety of double salts, which, according to Berlin, are principally of two types, containing either 1 atom of oxalate of chromium combined with 1 of the other oxalate; or of 1 and 3; there being only one instance of a combination of 1 atom of oxalate of chromium with 2 of another oxalate, namely, in the case of soda. (BERZELIUS, *Lehrbuch*, iii. 1087.)

*Oxalate of Ammonia and Chromium*.  $3[NH_4 O, C_2 O_3] + Cr_2 O_3, 3C_2 O_3 + 5HO$ . This is a *blue* salt, which forms small micaceous crystals: it is very soluble: it contains 10·72 *per cent.* of water. There is also a *red* ammonio-oxalate of chromium, forming brilliant crystals =  $NH_4 O, C_2 O_3, + Cr_2 O_3, 3C_2 O_3 + 8HO$ : it contains 24·9 *per cent.* of water.

*Oxalate of Potassa and Chromium*.  $3[KO, C_2 O_3] + Cr_2 O_3, 3C_2 O_3 + 6HO$ . This salt, first described by Gregory, and examined in reference to its optical properties by Brewster, (*Phil. Trans.*, 1835,) is prepared by dissolving together in hot water 1 part of bichromate of potassa, 2 parts of binoxalate of potassa, and 2 parts of oxalic acid; carbonic acid gas is evolved in consequence of the deoxidation of the chromic acid, and on evaporation the double salt forms prismatic crystals which are black by reflected light, but of a splendid blue by transmitted light, when sufficiently thin to be translucent. When strongly dried, they lose 11·7 *per cent.* of water. The oxide of chromium cannot be completely precipitated from the solution of this salt by an alkaline carbonate, and only a small portion of the oxalic acid is thrown down from it by chloride of calcium. When ignited, carbonic acid escapes, and the residuary salt is a mixture of 2 atoms of chromate and 1 atom of carbonate of potassa, entirely soluble in water, and containing no oxide of chromium. (GRAHAM.) This salt is soluble in 5 parts of water at 60°: it is insoluble in alcohol, which throws it down in the form of a green powder from its aqueous solution. It is precipitated by lime, and by baryta water, the resulting precipitate being a mixture of hydrated oxide of chromium with the oxalate of the earth.

A red *potassio-oxalate of chromium* =  $KO, C_2 O_3, + Cr_2 O_3, 3C_2 O_3, + 10HO$ , is obtained by gradually adding 55 parts of pulverised oxalic acid to a concentrated boiling solution of 19 parts of bichromate of



potassa, and when the effervescence has ceased, allowing the liquor to cool slowly. The boiling solution is greenish-black, but becomes red on cooling, and deposits a garnet-red crystalline crust. This salt is soluble in 10 parts of water at  $60^{\circ}$ . Evaporated in a water-bath, it leaves an amorphous green residue. Alcohol produces a red crystalline precipitate in its aqueous solution, which deliquesces on exposure to air. At  $250^{\circ}$  this salt loses 17.3 *per cent.*, = 7 atoms of water, retaining 3 in permanent combination.

*Oxalate of Soda and Chromium*,  $3[\text{NaO}, \text{C}_2\text{O}_3] + \text{Cr}_2\text{O}_3, 3\text{C}_2\text{O}_3, + 10\text{HO}$ , forms six-sided rhombic prisms or tables, black by reflected but dark-blue by transmitted light; they effloresce and become violet-colored on exposure to dry air, and are readily soluble in water; alcohol added to the aqueous solution, causes a precipitate of a greenish blue color and and syrupy consistence. When a solution of this salt is mixed with oxalate of soda, and left to spontaneous evaporation, small blue crystals are formed =  $2[\text{NaO}, \text{C}_2\text{O}_3] + \text{Cr}_2\text{O}_3, 3\text{C}_2\text{O}_3, + 10\text{HO}$ .

*Oxalate of Lime and Chromium*.  $3[\text{CaO}, \text{C}_2\text{O}_3] + \text{Cr}_2\text{O}_3, 3\text{C}_2\text{O}_3, + 18\text{HO}$ . This double salt is formed when freshly precipitated oxalate of lime is boiled in a concentrated solution of oxalate of chromium; or when oxalic acid is added to a boiling solution of chromate of lime, in which case the oxalate of lime not required for the formation of the double salt is precipitated. The hot liquor gradually deposits a dark-blue magma, which, when washed upon a filter, leaves a red crystalline salt, becoming a rose-colored crust on drying. It requires 200 parts of cold water for solution, but is much more soluble in boiling water, and does not again separate till evaporated to the consistence of syrup, when it forms red scales. If, however, the evaporation be conducted in a water-bath, a green amorphous mass is obtained, which is very soluble in water, but which, when so dissolved, soon reverts to the violet-colored modification, and yields the red scales. When boiled with a large quantity of water, this salt suffers a partial decomposition, oxalate of lime separates, and the liquor then retains an excess of oxalate of chromium; but when evaporated the red salt separates, and oxalate of chromium remains in the mother-liquor. If the boiled solution, after it has deposited its precipitate, be filtered, and when cold mixed with alcohol, a dark-red magma separates, whilst oxalate of chromium remains in solution. This magma deliquesces into a dark-brown liquor, and lets fall a red pulverulent deposit. This double oxalate contains 33.84 *per cent.* of water. Dried at  $212^{\circ}$ , it loses 23.8 *per cent.* of water = 16 atoms, and becomes pale blue; it retains the two remaining atoms of water, even when dried at  $285^{\circ}$ . (BERZELIUS, *Lehrbuch*, iii. 1090.)

*Oxalate of Baryta and Chromium*, is formed by boiling oxalate of baryta in a boiling solution of oxalate of chromium; on cooling, blue crystals are deposited.

*Oxalate of Magnesia and Chromium*.  $\text{MgO}, \text{C}_2\text{O}_3, + \text{Cr}_2\text{O}_3, 3\text{C}_2\text{O}_3 + 10\text{HO}$ . If oxalic acid be added to a hot solution of chromate of magnesia till the chromic acid is reduced to oxide, half of the magnesia is precipitated in the form of oxalate, and a violet-colored solution is obtained, which, if immediately filtered and left to spontaneous evaporation, yields red crystals resembling those of the corresponding potassa salt. But if the solution be boiled with the precipitated oxalate of



magnesia, a part is again dissolved, and on filtering and leaving the solution to spontaneous evaporation, small blue prismatic crystals are obtained  $= 3[\text{MgO}, \text{C}_2 \text{O}_3] + \text{Cr}_2 \text{O}_3, 3\text{C}_2 \text{O}_3$ . (BERLIN.)

*Oxalate of Molybdenum.* The *protoxalate* is dark-gray, but black when dry; it is little soluble in excess of oxalic acid. The *peroxalate* may be obtained in very dark-blue crystals, yielding a red solution, from which ammonia throws down a red *basic* salt, insoluble in excess of ammonia. Molybdic acid yields a colorless solution in oxalic acid, which, when evaporated, becomes at first gelatinous, and then crystalline; it is soluble in water and alcohol. These oxalates of molybdenum all yield double salts with oxalate of potassa. (BERZELIUS.)

*Oxalate of Titanium* falls as a curdy hydrated precipitate, when a solution of titanium is heated with oxalic acid: it dissolves in excess of the acid, and consists, according to Rose, of 6 atoms of oxide of titanium, 1 of oxalic acid, and 6 of water.

*Oxalate of Columbium.* According to Wollaston, the recently-precipitated hydrated columbic acid dissolves in oxalic acid; but Gahn, Berzelius, and Eggertz state, that only a trace of the acid is so dissolved, but that binoxalate of potassa readily takes it up and forms with it a double salt, from which the alkalis throw down columbic acid.

*Oxalate of Mercury* is precipitated from the nitrates by oxalic acid. The *protoxalate*,  $\text{Hg}_2 \text{O}, \text{C}_2 \text{O}_3$ , is scarcely soluble, and detonates slightly when heated. It was once supposed to exist in Howard's fulminating mercury, but this is not the case. It forms a double salt with oxalate of potassa. *Peroxalate of Mercury*, (oxalate of the red oxide of mercury,)  $\text{HgO}, \text{C}_2 \text{O}_3$ , is obtained by precipitating the peracetate of mercury by a solution of oxalic acid or of an oxalate: it is white and insoluble, and detonates slightly when heated. Boiled in water an acid solution is obtained, and the residue is basic. It is insoluble in alcohol, and but very slightly soluble in ether. It is soluble in hot hydrochloric and nitric acid. It forms a basic double salt with ammonia  $= [\text{HgO}, \text{C}_2 \text{O}_3 + 3\text{HgO} + \text{NH}_3]$  (BERZELIUS.)

*Oxalate of Silver*,  $\text{AgO}, \text{C}_2 \text{O}_3$ , is an insoluble white powder, which blackens when exposed to light. It is precipitated on adding oxalic acid to nitrate of silver, and is soluble in nitric acid. It detonates slightly when violently struck upon an anvil; when heated, it becomes electric, and also slightly explodes, evolving water and carbonic acid, and leaving metallic silver. It forms a double salt with oxalate of potassa  $= \text{KO}, \text{C}_2 \text{O}_3 + \text{AgO}, \text{C}_2 \text{O}_3$ .

When a stream of hydrogen gas is passed over oxalate of silver heated to  $212^\circ$ , a pale brown compound is obtained  $= \text{Ag}_2 \text{O}, \text{C}_2 \text{O}_3, \text{HO}$ . It explodes when heated to  $285^\circ$ .

*Oxalate of Alumina*,  $\text{Al}_2 \text{O}_3, 3\text{C}_2 \text{O}_3$ , is formed by dissolving newly-precipitated alumina in oxalic acid; it does not crystallise, but affords, on evaporation, a gelatinous mass, which deliquesces on exposure. This is probably a *binoxalate*, for Berzelius states that the neutral oxalate is insoluble.

An *oxalate of potassa and alumina* has been formed, containing 3 equivalents of oxalate of potassa, 1 of oxalate of alumina, and 6 of water; its formula being  $3[\text{KO}, \text{C}_2 \text{O}_3] + \text{Al}_2 \text{O}_3, 3\text{C}_2 \text{O}_3, + 6\text{HO}$ . The corresponding *soda oxalate* crystallizes with  $10\text{HO}$ . (GRAHAM.)

*Oxalate of Glucina* is soluble in water, and has a more decidedly sweet taste than any other of the salts of glucina.

*Oxalate of Yttria*,  $Y, C_2 O_3$ , is insoluble in water, and oxalic acid or oxalate of ammonia are the best precipitants of this earth. The *oxalate of potassa and yttria* is also an insoluble double salt. (See MOSANDER, on the separation of yttria from the oxides of Erbium and Terbium. BERZELIUS, *Lehrbuch*, ii. 178.)

Several of the double oxalates have been described by H. Reece. (*Comptes Rendus*, Nov. 1845.)

XI. SACCHARIC ACID. HYDROXALIC ACID. OXALHYDRIC ACID.  $C_6 H_4 O_7$ . This acid was first discovered by Guérin Varry, (*Ann. Ch. et Ph.*, lii. 318;) it is formed, together with oxalic acid, during the action of nitric acid upon sugar, gum, and other substances; it was originally noticed by Scheele, who considered it as identical with malic acid. Erdmann, who repeated Guérin Varry's experiments in 1837, regarded this acid as isomeric with tartaric acid, and called it *metatarlaric acid*, and shortly afterwards, Hess gave it the name of *Saccharic acid*, a name, however, which had before been applied to the oxalic acid; its properties have recently been examined by Heintz. (*Proceedings of the Royal Academy of Berlin*, Jan. 1844.)

Guérin obtained this acid by mixing 1 part of gum arabic with 2 of nitric acid diluted with half its weight of water, in a retort of four times the capacity of that of the mixture, and connected with a tubulated receiver; heat is applied till nitrous vapors begin to appear; it is then withdrawn, and a large quantity of nitrous gas succeeds; when this ceases, the liquor is boiled for an hour, then diluted with 4 parts of water, saturated by ammonia, and a solution of nitrate of lime is then added to precipitate oxalic acid: the solution, which is now of an orange color, is filtered and precipitated by acetate of lead; the precipitate is washed upon a filter till the washings no longer are discolored by sulphuretted hydrogen, and is then decomposed either by a stream of that gas, or by sulphuric acid diluted with 6 weights of water; the acid thus obtained is evaporated by a gentle heat, and, when sufficiently concentrated, is neutralized by ammonia, and evaporated till it begins to crystallise. The crop of crystals which it affords, and which are dark-colored, are dissolved and treated by animal charcoal; the decolorized solution is then precipitated again by acetate of lead, and the precipitate is decomposed as before: the acid liquor now obtained is cautiously evaporated till it acquires the consistency of syrup, and the evaporation is completed in vacuo, till the residuary liquor begins to acquire a yellow tint.

Trommsdorf's process for obtaining saccharic acid is as follows:—He heats a mixture of equal parts of sugar and nitric acid (specific gravity 1.2) till it begins to effervesce; abundance of gas is evolved, and the liquid becomes thick and yellow; it is then diluted with water, and saturated by chalk, the excess of which, and the precipitated oxalate of lime, are removed by filtration; the filtered liquor is concentrated by evaporation and mixed with alcohol, which precipitates the *saccharate of lime*; this is collected, redissolved, filtered through charcoal, and decomposed by acetate of lead; the resulting *saccharate of lead* is decomposed as before by sulphuretted hydrogen: to get it colorless, the acid must be



saturated by soda, again thrown down by lead, and this decomposed as before. 8 ounces of sugar yield about 1 ounce of the acid. (*Ann. Ch. et Ph.*, liv. 208.)

According to Heintz, hydroxalic acid is formed almost free from oxalic acid, by acting by 3 parts of nitric acid (sp. gr. 1·25 to 1·30) upon 1 of sugar, taking care that the temperature does not exceed 122°, at which is to be retained, and stirred till the green color resulting from nitrous acid disappears: the liquor is then diluted with half its volume of water, saturated by potassa, and mixed with acetic acid, so that the odor of that acid may predominate; in the course of a few days, it begins to deposit crystals of acid saccharate of potassa, the formation of which may continue for some weeks; this salt is removed and dried on blotting-paper; it is then dissolved in boiling water, and recrystallised, and this operation is repeated till the crystals, originally yellow, are rendered colorless. Scholvin recommends adding, from time to time, during the decomposition of the sugar by the acid, a little alcohol, which prevents the formation of oxalic acid, even when the temperature rises above 122°, and he uses twice the quantity of acid directed by Heintz.

The acid saccharate of potassa is then carefully rendered neutral, and its solution precipitated by a salt of baryta, lead, or cadmium. When a salt of lead is used, the precipitate is seldom free from the acid of the lead-salt; and baryta is objectionable, inasmuch as, when it is separated in the form of sulphate, a slight excess of sulphuric acid is apt to render the saccharic acid brown, or else a little saccharate of potassa remains in excess, which, dissolved in the saccharic acid, crystallises during concentration, a property which led to the statement that saccharic acid is crystallisable. Heintz, therefore, prefers decomposing the saccharate of potassa by a neutral salt of cadmium; the precipitate is well washed, and decomposed by excess of sulphuretted hydrogen; the result is a solution of pure saccharic acid, from which the sulphuretted hydrogen may be expelled, at first by a gentle heat, and then in a vacuum over sulphuric acid, where the evaporation may be continued to dryness.

Saccharic acid thus obtained is a hard, amorphous, colorless, inodorous substance, very sour, and not volatile, but decomposed by heat with a carbonaceous residue. It is deliquescent, and very soluble in water and alcohol, but sparingly soluble in ether. In this state it is probably in combination with an atom of water; in its anhydrous state, as it exists combined with bases = Sac, it consists of

|                               |   |     |    |     |        |
|-------------------------------|---|-----|----|-----|--------|
| Carbon .....                  | 6 | ... | 36 | ... | 37·50  |
| Hydrogen .....                | 4 | ... | 4  | ... | 4·16   |
| Oxygen .....                  | 7 | ... | 56 | ... | 58·34  |
| <hr/>                         |   |     |    |     |        |
| Anhydrous saccharic acid..... | 1 |     | 96 |     | 100·00 |

Saccharic acid is not altered by exposure to air, when in concentrated aqueous solution; but its dilute solution becomes mouldy. By boiling with nitric acid it is converted into oxalic acid; heated with sulphuric acid it is blackened, and sulphurous acid is evolved; it is not altered by boiling with solution of caustic potassa, but when fused with moistened hydrate of potassa it forms, at a temperature of about 480°, 1 atom of oxalic acid and 1 atom of acetic acid:  $[C_6 H_4 O_7 = C_2 O_3 + C_4 H_3 O_3 + HO]$ . Nitrate of silver is not precipitated by saccharic acid, but if the

solution be supersaturated by ammonia, the precipitate which first falls is redissolved, and metallic silver is after a time deposited; when the mixed solution is boiled, the glass becomes coated by metallic silver. Many of the sparingly soluble salts of this acid subside in the cold as flocculent precipitates, but cohere on boiling into a tenacious mass, and by longer boiling become solid. Neither the acid itself, nor the alkaline saccharates, diffuse when heated the odor of burned sugar, which distinguishes them from tartaric acid and the tartrates.

*Saccharate of Ammonia*,  $\text{NH}_4\text{O}, \overline{\text{Sac}}$ , dries *in vacuo* to a gummy mass. The *bisaccharate*  $[\text{NH}_4\text{O}, \overline{\text{Sac}} + \text{HO}, \overline{\text{Sac}}]$  is formed either by heating the neutral salt, or adding acid to it; it crystallizes in prisms, which are sparingly soluble in water.

*Saccharate of Potassa*,  $\text{KO}, \overline{\text{Sac}}$ , is a very soluble, deliquescent, and difficultly crystallisable salt: it is anhydrous. *Bisaccharate* of potassa,  $\text{KO}, \overline{\text{Sac}} + \text{HO}, \overline{\text{Sac}}$ , is best obtained by adding an equivalent of acid to the neutral salt. It much resembles bitartrate of potassa, but when heated it puffs up, and does not exhale the peculiar odor of burned tartar. Between  $32^\circ$  and  $45^\circ$  it requires from 88 to 90 parts of water for solution; but it is very soluble in boiling water.

*Saccharates of Soda*. Both the neutral and acid salt yield, on evaporation, gumlike, deliquescent masses.

*Saccharate of Lime*,  $\text{CaO}, \overline{\text{Sac}}, \text{HO}$ , when precipitated from cold solutions, is flocculent, but it crystallizes from boiling liquors; it retains an atom of water.

*Saccharate of Baryta*,  $\text{BaO}, \overline{\text{Sac}}$ , forms an anhydrous flocculent precipitate, crystalline when thrown down from boiling solutions.

*Saccharate of Magnesia*, when formed by double decomposition, does not fall till the liquor is evaporated, when it forms a lamellar deposit. It forms a double salt with saccharate of potassa,  $[\text{KO } \overline{\text{Sac}} + \text{MgO } \overline{\text{Sac}}, 3\text{HO}]$ , obtained by boiling magnesia with excess of bisaccharate of potassa; it does not dissolve, but forms a crystalline powder, whilst the bisaccharate is rendered neutral; it contains 3 atoms of water of crystallization, which may be expelled by heat. This salt is sparingly soluble in boiling water, and is deposited in crystalline grains on cooling: it is soluble in caustic potassa.

*Saccharate of protoxide of Iron* is formed by dissolving iron in the acid; on evaporation *in vacuo* it remains as a gumlike mass. The *saccharate of peroxide of iron* is obtained by digesting the moist and recently precipitated peroxide of iron in a solution of saccharic acid: it forms a yellow liquor.

*Saccharate of Zinc* may be obtained by digesting the metal in the acid; or better, by double decomposition at a boiling heat. This salt is somewhat soluble in boiling water, and is deposited on cooling in acicular crystals  $= \text{ZnO}, \overline{\text{Sac}}, \text{HO}$ .

*Saccharate of Cadmium*,  $\text{CdO}, \overline{\text{Sac}}$ , when precipitated by double decomposition from cold solutions, is flocculent and sparingly soluble, becoming somewhat tenacious when heated. If the solution be boiling, the salt falls in the form of an anhydrous crystalline powder.

*Saccharate of Lead*,  $\text{PbO}, \overline{\text{Sac}}$ , is obtained by saturating an aqueous



solution of saccharic acid with freshly precipitated and moist carbonate of lead, added in small successive portions: the first generally dissolve, but afterwards the saccharate falls in proportion as saturation ensues, in the form of a white powder, very sparingly soluble in boiling water. When a salt of lead is mixed with an alkaline saccharate, the precipitate which falls is a double salt. In this way, with nitrate of lead and saccharate of potassa, we obtain  $\text{PbO}, \text{NO}_5 + \text{PbO}, \overline{\text{Sac}}$ . It is almost insoluble, and crystalline when thrown down from boiling solutions; it explodes previous to ignition, with a faint light, and becomes black from separated carbon. The precipitate resulting from the mixture of solutions of acetate of lead and saccharate of potassa has not been accurately analysed: it contains acetate of lead, and appears to be a basic acetate and saccharate, mixed with carbonate of lead formed during its production. Thaulow and Liebig, who represented the saccharic acid as *pentabasic*, attributed to this salt the formula  $5\text{PbO}, + \text{C}_{12} \text{H}_{10} \text{O}_{11}$ .

*Saccharate of Bismuth* is obtained when a diluted solution of nitrate of bismuth is precipitated by saccharate of potassa; it is insoluble in water, and sparingly soluble in acids. Heintz could not obtain it of uniform composition, but it always appeared to be basic.

*Saccharate of Copper* was obtained in the form of a green precipitate, by digesting hydrated oxide of copper in saccharic acid; it was gradually dissolved by water on washing it upon a filter, and on evaporating the filtered solution, it remained as a green amorphous salt. It cannot be obtained by double decomposition.

*Saccharate of Silver*,  $\text{AgO}, \overline{\text{Sac}}$ , is formed by mixing a solution of nitrate of silver with one of acid saccharate of potassa; it is also precipitated by adding nitrate of silver to a solution of neutral saccharate of potassa, leaving the latter in excess; if the saccharate be dropped into the salt of silver it blackens it. This salt is a crystalline powder, soluble in hot water, from which it is afterwards deposited in crystalline scales. It is neutral and anhydrous. It readily dissolves in ammonia, but the solution soon deposits metallic silver, and, if boiled, the vessel is lined with a brilliant coating. A solution of nitrate of silver is not precipitated by saccharic acid. (BERZELIUS, *Lehrbuch*, iv. 610. *Chem. Gaz.*, 1844, p. 255.)

XII. TARTARIC ACID. *Tartrylic acid*.  $\text{C}_8 \text{H}_4 \text{O}_{10} + 2\text{HO} = \overline{\text{Tar}}, 2\text{HO}$ . Scheele first obtained crystallized tartaric acid in 1770, (*Stockholm Transactions*), by the decomposition of tartar. It exists *free* in many fruits, especially in tamarinds, grapes, and the pepper plant; as *tartar*, also in grapes and tamarinds, in mulberries, samphire, &c.: in the root of wheat (*Triticum repens*), and of dandelion (*Leontodon Taraxacum*), in the berries of sumach (*Rhus coriaria*), and in the rhubarb plant, the potato, and Iceland moss; as *tartrate of lime*, in squills, madder root, quassia wood, the fruit of *Rhus typhinum*, and the tubercles of *Helianthus tuberosus*. (GMELIN.)

Tartaric acid is generally obtained from the *bitartrate of potassa* or *purified tartar* by the process originally devised by Scheele: 4 parts of finely-powdered tartar are thoroughly mixed with 1 part of pulverized chalk, and the mixture is thrown by small portions at a time into about

10 parts of water, which is kept boiling during the process; when the effervescence is over, the whole is stirred together, and left to subside. The liquor, which is a solution of *neutral* tartrate of potassa, is then poured off the sediment, which is *tartrate of lime*, the lime having abstracted and combined with half the tartaric acid of the bitartrate of potassa. A solution of chloride of calcium is then added to the neutral liquor as long as a precipitate ensues, and in this way an additional quantity of tartrate of lime is obtained, which is washed and mixed with the first product, while chloride of potassium remains in the solution. The whole product of tartrate of lime having been well washed, is next to be decomposed by a proper quantity of dilute sulphuric acid, which, combining with the lime, throws down sulphate of lime, whilst the tartaric acid remains in aqueous solution, and is poured or filtered off. The tartrate of lime thus resulting from the decomposition of 4 parts of tartar, requires for its decomposition 2.1 parts of oil of vitriol; but in practice rather more is employed, inasmuch as the tartaric acid crystallizes better in a mother-liquor holding a slight excess of sulphuric acid, and the presence of any undecomposed tartrate of lime in the mother-liquor is very inconvenient. The oil of vitriol should be diluted with 4 parts of water, and well mixed and digested with the moist tartrate of lime. When the decomposition is complete, the solution containing the tartaric acid is strained off from the remaining sulphate of lime, and concentrated by evaporation, during which some sulphate of lime is deposited: the clear liquor is then very slowly evaporated in a warm place, when crystals of tartaric acid are gradually formed. The first crystals are usually brown, so that they require to be redissolved and digested with a little purified animal charcoal, till the liquor is colorless; it is then again evaporated and crystallized.

Tartaric acid may also be obtained by neutralizing 1 part of tartar by carbonate of potassa, and digesting the solution for an hour with 8 parts of quicklime, decanting the liquor (which contains caustic potassa), washing the residue with dilute acetic or hydrochloric acid to free it from excess of lime, and then decomposing it by dilute sulphuric acid, as above. (OSANN.) Dr. Henry states, that in this process the free potassa prevents the precipitation of the tartrate of lime.

Fabbroni obtained tartaric acid by adding excess of powdered tartar to a boiling mixture of 1 part of sulphuric acid and 3 of water; the solution, on cooling, deposits some tartar and sulphate of lime, from which it is poured off, and evaporated to a small bulk; alcohol is then added, which dissolves out the tartaric acid, and leaves bisulphate of potassa. (*Ann. Ch. et Ph.*, xxv. 9.)

Tartaric acid may also be obtained by decomposing *tartrate of lead*, diffused through water, by sulphuretted hydrogen.

Crystallized tartaric acid is intensely sour: its specific gravity is about 1.7; it is generally semitransparent, and of complicated forms which appear to be modifications of a rhombic prism. (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 118; PECLET, *Ann. Ch. et Ph.*, xxxi. 78.) The crystals acquire electric polarity by heat, in this respect resembling the tourmalin. It is not altered in a dry atmosphere, but in humid air it tends slightly to deliquescence. Water dissolves 1.5 its weight of tartaric acid at 60°, and twice its weight at 212°. The concentrated



solution has the consistence of syrup. The solubility of this acid is, however, variously stated, and it is not easy, under common circumstances, to dissolve more than 1 part of the crystals in 4 or 5 of water ; but when a boiling solution is cooled to 60°, it retains much more. It is also soluble in alcohol. The dilute aqueous solution of tartaric acid soon becomes mouldy, and suffers decomposition. Boiled in nitric acid, tartaric acid is partly converted into oxalic acid; and sulphuric acid converts it into acetic acid. It becomes converted into oxalic and acetic acid by fusion with potassa. It is transformed by the action of peroxide of manganese or of lead into formic and carbonic acid, a tartrate of the protoxide being at the same time formed. It reduces the salts of the peroxide of gold.

Tartaric acid is distinguished by the white granular precipitate which it produces when added in excess to solutions containing potassa. If these solutions be very dilute, the crystalline precipitation is accelerated by the addition of alcohol, bitartrate of potassa being almost insoluble in a mixture of alcohol and water. It produces a white precipitate, soluble in excess of acid, in lime, baryta, and strontia-water, and in acetate of lead. It is used in calico-printing, and is much employed as a cheap substitute for citric acid in lemonade and effervescent solutions; in the laboratory it is used as a test of the salts of potassa, and to prevent the precipitation of certain oxides, as that of antimony, and the titanio acid.

The tartaric acid of commerce is apt to be contaminated by traces of sulphuric acid, and of lead, the presence of the latter metal being derived from the leaden vessels used in its preparation upon the large scale. To detect sulphuric acid, chloride of barium may be used; if added in excess, or if the solution of tartaric acid under examination be concentrated, tartrate of baryta will fall; but the presence of sulphuric acid in the precipitate is easily recognized by its insolubility in hydrochloric acid, which acid dissolves pure tartrate of baryta. Sulphuretted hydrogen is the test of the presence of lead.

Tartaric acid is usually regarded as *bibasic*, its formula being  $C_8H_4O_{10} + 2HO$ . The components, therefore, of the *anhydrous acid*, as it exists in combination with certain bases, will be

|                               |    |      |     |      |        |             |
|-------------------------------|----|------|-----|------|--------|-------------|
|                               |    |      |     |      |        | Berzelius.  |
| Carbon .....                  | 8  | .... | 48  | .... | 36.37  | .... 35.980 |
| Hydrogen .....                | 4  | .... | 4   | .... | 3.03   | .... 3.807  |
| Oxygen .....                  | 10 | .... | 80  | .... | 60.60  | .... 60.213 |
| <hr/>                         |    |      |     |      |        | <hr/>       |
| Anhydrous tartaric acid ..... | 1  |      | 132 |      | 100.00 | 100.000     |

The *crystallized acid* contains

|                                       |    |     |     |     |     |       |                                       |   |     |     |     |           |     |        |
|---------------------------------------|----|-----|-----|-----|-----|-------|---------------------------------------|---|-----|-----|-----|-----------|-----|--------|
|                                       |    |     |     |     |     |       |                                       |   |     |     |     | Berzelius |     |        |
| Carbon .....                          | 8  | ... | 48  | ... | 32  | } = { | Anhydrous acid                        | 1 | ... | 132 | ... | 88        | ... | 88.06  |
| Hydrogen .....                        | 6  | ... | 6   | ... | 4   |       | Water                                 | 2 | ... | 18  | ... | 12        | ... | 11.94  |
| Oxygen .....                          | 12 | ... | 96  | ... | 64  |       |                                       |   |     |     |     |           |     |        |
| <hr/>                                 |    |     |     |     |     |       |                                       |   |     |     |     |           |     |        |
| Crystallized tar-<br>taric acid ..... | 1  |     | 150 |     | 100 | } = { | Crystallized tar-<br>taric acid ..... | 1 |     | 150 |     | 100       |     | 100.00 |
| <hr/>                                 |    |     |     |     |     |       |                                       |   |     |     |     |           |     |        |

*Tartrates.* This acid, regarded as bibasic, forms two classes of salts; in one, which may be termed the *neutral tartrates*, 2 atoms of base are combined with 1 atom of acid  $[2MO + Tar]$ ; in the other, or in the

*acid tartrates* (bitartrates), 1 atom of fixed base is replaced by 1 atom of water, their formula being  $[\text{MO}, \text{HO}, + \overline{\text{Tar}}]$ .

Tartaric acid also forms two descriptions of *double salts*; in one of these the 2 atoms of fixed base are two different protoxides,  $[\text{MO}, m\text{O} + \overline{\text{Tar}}]$ ; in the other, 1 of the atoms of the fixed base is replaced by 1 atom of a sesquioxide  $[\text{MO}, m_2\text{O}_3, + \overline{\text{Tar}}]$ : it is obvious that these latter salts are in fact *basic*, inasmuch as 1 atom of the *sesquioxide*  $= m_2\text{O}_3$  generally neutralizes as much acid as 3 atoms of a *protoxide*  $= \text{MO}$ .

Tartaric acid has a remarkable tendency to the formation of these double salts. The tartrates are easily decomposed by heat, evolving water and carbonic oxide, carbonic acid, and carburetted hydrogen, together with an oily product; the residue is either a metal, or its oxide, or carbonate, mixed with charcoal. The tartrates with excess of acid yield a peculiar odor when burned, resembling that of burned sugar.

*Tartrate of Ammonia*,  $2\text{NH}_4\text{O}, \overline{\text{Tar}} + 2\text{HO}$ , forms very soluble prismatic crystals, of a cooling taste; they effloresce, and become sour by exposure to air. The addition of tartaric acid to the aqueous solution of the neutral salt, produces a precipitate of a difficultly-soluble acid tartrate, or *bitartrate* of ammonia,  $= \text{NH}_4\text{O}, \text{HO}, \overline{\text{Tar}}$ . When a saturated solution of tartaric acid is added to strong liquid ammonia in such proportions as to form this tartrate, the liquids concrete with great rise of temperature.

*Tartrate of Potassa*,  $2\text{KO}, \overline{\text{Tar}}$ , is formed by saturating the excess of acid in *tartar*, by potassa. The resulting salt is soluble in less than twice its weight of water, (hence, in opposition to the acid tartrate, it is termed *soluble tartar*.) It crystallizes in four and six-sided prisms with dihedral summits, but its primitive form is a right rhomboidal prism. (BROOKE, *Ann. of Phil.*, N.S., vii. 161.) Its taste is saline and bitter, and it is used in medicine, (formerly under the name of *Tartarus tartarisatus*,) as an aperient. It is slightly deliquescent, and almost insoluble in absolute alcohol. Most acids occasion a precipitate of acid tartrate of potassa when added to the aqueous solution of this salt. Tartrate of potassa is *anhydrous*, and consists of

|                     |   |     |       |     |       | Thomson. | Berzelius. |
|---------------------|---|-----|-------|-----|-------|----------|------------|
| Potassa .....       | 2 | ... | 96    | ... | 42.1  | 42       | 41.31      |
| Tartaric acid ..... | 1 | ... | 132   | ... | 57.9  | 58       | 58.69      |
| <hr/>               |   |     | <hr/> |     | <hr/> | <hr/>    | <hr/>      |
| Tartrate of potassa | 1 |     | 228   |     | 100.0 | 100      | 100.00     |

*Bitartrate of Potassa. Supertartrate of Potassa. Tartar.*  $\text{KO}, \text{HO}, \overline{\text{Tar}}$ . This substance exists in considerable abundance in the juice of the grape, and is deposited in wine casks in the form of a crystalline incrustation, called *argol*, or *crude tartar*. It is purified by solution and crystallization, which renders it perfectly white. When in fine powder, it is termed *cream of tartar*. The purification of *tartar* at Montpellier is performed as follows:—It is first dissolved in boiling water, and crystallized; these crystals are then boiled with one-twentieth their weight of pipe-clay, (and the same quantity of animal charcoal?) which absorbs the coloring matter, and falls as an insoluble sediment, the crystals of pure tartar separating afterwards upon the surface of the



liquor, and upon the sides and bottom of the boiler; the term *cream of tartar* was originally applied to the imperfectly crystallized superficial crust. The details of this process are described by M. Fizes, (*Mémoires de l'Académie*, 1725,) and it is still carried on upon the same plan. The Venetian process for the purification of tartar consists in the separation of the grosser impurities by one or two preliminary solutions and crystallizations, after which, white of egg and wood ash are added to the boiling solution of the crystals, and the impurities skimmed off during the effervescence which ensues. (DESMARET, *Jour. de Phys.*, i. 67.)

Bitartrate of potassa may be formed artificially, by adding excess of tartaric acid to a solution of potassa. The mixture presently deposits crystalline grains, and furnishes a striking example of diminution of solubility by increase of acid in the salt. Upon this circumstance the use of tartaric acid as a *test* for potassa depends, for soda forms an easily soluble supertartrate, and consequently affords no precipitate.

Its crystals, which are irregular six-sided prisms, terminated by hexahedral summits, or triangular prisms with dihedral summits, have been described by Wollaston, (*Thomson's Annals*, x. 37,) and by Brooke, (*Ann. of Phil.*, N. S., vii. 161.) They include 1 equivalent of constitutional water, which is not separable at a heat much below that at which the acid of the salt begins to be decomposed. They are hard, and taste gritty and subacid. Their components are

|                                |   |      |     |      |        |
|--------------------------------|---|------|-----|------|--------|
| Potassa .....                  | 1 | .... | 48  | .... | 25·39  |
| Water .....                    | 1 | .... | 9   | .... | 4·76   |
| Tartaric acid .....            | 1 | .... | 132 | .... | 69·85  |
| <hr/>                          |   |      |     |      |        |
| Supertartrate of potassa ..... | 1 |      | 189 |      | 100·00 |

The specific gravity of this salt is 1·95. It is soluble in 184 parts of water at 68°; and in 18 parts at 212° (LIEBIG); in 204 parts at 66°, in 89 parts at 76°, in 38 parts at 122°, in 22 parts at 166°, and in 15 parts at 212°. (BRANDES and WARDENBURG.) It is rendered much more soluble by the addition of boracic acid or of borax, as was first observed by Le Fevre. (*Mém.*, Paris, 1732.) 2 parts of borax, and 5 of crystals of tartar in powder, are soluble in about 6 times their weight of boiling water; on evaporating the solution to the consistency of honey, the residue concretes into *Le Fevre's soluble cream of tartar*, or *sal-gummosum*. It is the *tartarus boraxatus* of some old writers. When exposed to heat, tartar fuses, blackens, and is decomposed, and carbonate of potassa, mixed with charcoal, is the remaining result. According to Brunner, 100 parts of tartar leave a residue of 8·75 parts of charcoal, and 31·25 of carbonate of potassa. Provided the tartar be free from lime, which however is seldom the case, this furnishes a good process for obtaining pure *carbonate of potassa*. By destructive distillation, Fourcroy and Vauquelin obtained the following residuary substances from 1000 grains of crystals of tartar. (*Ann. de Chim.*, Lxiv. 43.)

|                            |     |  |                          |      |
|----------------------------|-----|--|--------------------------|------|
| Carbonate of potassa ..... | 350 |  | Alumina .....            | 0·25 |
| Carbonate of lime .....    | 6   |  | Iron and manganese ..... | 0·75 |
| Silica .....               | 1·2 |  |                          |      |

The aqueous solution of tartar becomes mouldy when exposed to air, and the tartaric acid being entirely decomposed, leaves a weak

solution of carbonate of potassa. Tartar sometimes acts as a simple acid, and dissolves several oxides which are insoluble in many other acids; hence Gay Lussac has suggested its use in certain analyses. (*Ann. Ch. et Ph.*, iii. 281.) By the action of excess of caustic potassa, at high temperatures, tartar is converted into oxalate of potassa. The component parts of tartar render it an excellent flux in the reduction of metallic ores upon a small scale, its alkali promoting their fusion, and the carbonaceous matter tending to reduce the oxides. Tartar is sometimes adulterated by the addition of pounded quartz, and by calcareous spar; the former may be detected as an insoluble residue by boiling the powdered tartar with half its weight of carbonate of potassa, or of borax, in 8 parts of water; the latter produces effervescence with dilute hydrochloric acid. A small portion of tartrate of lime is almost always present in purified tartar; it separates in tufts of acicular crystals from the hot solution of the salt. Supertartrate of potassa is used in pharmacy, and is frequently employed by dyers as a mordant.

*Tartrate of Potassa and Ammonia*,  $\text{KO}, \text{NH}_4\text{O}, \overline{\text{Tar}}$ , is formed by saturating the excess of acid in tartar, with ammonia. It forms transparent four and six-sided prisms, very soluble in water, and which effloresce and lose ammonia by exposure to air.

*Tartrate of Soda*,  $2\text{NaO}, \overline{\text{Tar}} + 4\text{HO}$ , forms acicular crystals, soluble in about their own weight of water, and insoluble in absolute alcohol. They contain, according to Bucholz, 16 *per cent.* (4 equivalents) of water. When their aqueous solution is mixed with half their weight of tartaric acid, it yields small prismatic crystals of *bitartrate of soda*,  $= \text{NaO}, \text{HO}, \overline{\text{Tar}}, 2\text{HO}$ , of an acid taste, soluble in 8 parts of cold and 1·8 of boiling water, and containing about 15 *per cent.* (6 equivalents) of water of crystallization. (*Gehlen's Journ.*, v. 520.) Tartrate of soda is often formed extemporaneously by dissolving equal parts of powdered tartaric acid and of bicarbonate of soda, in separate portions of water, and then mixing the solutions; if taken during the effervescence, it forms a refreshing saline and slightly aperient draught.

*Tartrate of Potassa and Soda*,  $\text{KO}, \text{NaO}, \overline{\text{Tar}} + 10\text{HO}$ , is prepared by saturating the excess of acid in tartar, with carbonate of soda; it is the *Soda tartarizata* of the *Pharmacopœia*; it forms fine transparent prismatic crystals, having from 4 to 16 sides; they are generally formed in halves, and include 10 atoms of water (or, according to Mitscherlich, Schaffgottsch, and Thomson, only 8 atoms of water,  $= 25$  *per cent.*) They have been described by Brooke. (*Ann. of Phil.*, N. S., v. 451.) This salt has long been used in pharmacy as a mild aperient, under the name of *Rochelle Salt* and *Sel de Seignette*, having been first prepared at Rochelle by an apothecary by the name of Seignette. The crystals are soluble in about 3 parts of cold water, and consist of

|                     |       |     |       |     |       | Schulze. | Vauquelin.        |
|---------------------|-------|-----|-------|-----|-------|----------|-------------------|
| Potassa .....       | 1     | ... | 48    | ... | 15·9  | ...      | 14·3 Tartrate of  |
| Soda .....          | 1     | ... | 32    | ... | 10·6  | ...      | 13·3 potassa } 54 |
| Tartaric acid ..... | 1     | ... | 132   | ... | 43·7  | ...      | 41·3 Tartrate of  |
| Water .....         | 10    | ... | 90    | ... | 29·8  | ...      | 31·1 soda } 46    |
|                     | <hr/> |     | <hr/> |     | <hr/> |          | <hr/>             |
|                     | 1     |     | 302   |     | 100·0 |          | 100               |



*Tartrate of Lithia*,  $2\text{LO}, \overline{\text{Tar}}$ , is easily soluble; when its solution is evaporated it affords a white uncrystallized mass, opaque and not deliquescent. Excess of tartaric acid does not give a crystallizable bitartrate. *Tartrate of Potassa and Lithia*, formed by saturating tartar with carbonate of lithia, affords quadrangular prismatic crystals, easily soluble, and very slightly efflorescent. *Tartrate of Soda and Lithia* forms rectangular four-sided prisms, easily soluble, slightly efflorescent, and of a pure saline flavor. (C. GMELIN.)

*Tartrate of Lime*,  $2\text{CaO}, \overline{\text{Tar}} + 8\text{HO}$ , is very sparingly soluble in cold water; it is soluble in 600 parts of boiling water; it is produced by adding chalk to tartar, as in the process for obtaining tartaric acid, where it is decomposed by sulphuric acid; it is also thrown down on dropping a solution of tartaric acid into excess of lime water; but the neutral salts of lime are not precipitated by free tartaric acid. Tartrate of lime dissolves sparingly in excess of tartaric acid, and may be obtained from such solution in small silky crystals (which, according to Dulk, are a *bitartrate*). It is often contained in rough and purified tartar, and sometimes forms tufts of acicular crystals when tartar is saturated by bases. Dilute hydrochloric acid dissolves and decomposes it: but if this solution is saturated by ammonia, the tartrate of lime is reproduced, and crystallises after some hours in acute octohedra. Solution of potassa dissolves tartrate of lime, and when concentrated by evaporation becomes gelatinous, but liquifies on cooling. (DUMAS.) Tartrate of lime, after desiccation at  $212^\circ$ , consists of

|                   |   |      |     |      |        | Berzelius. | Gay Lussac<br>and Thenard. |
|-------------------|---|------|-----|------|--------|------------|----------------------------|
| Lime .....        | 2 | .... | 56  | .... | 21.54  | .... 21.64 | .... 22.423                |
| Tartaric acid ... | 1 | .... | 132 | .... | 50.77  | .... 50.55 | } .... 77.577              |
| Water .....       | 8 | .... | 72  | .... | 27.69  | .... 27.81 |                            |
| <hr/>             |   |      |     |      |        |            |                            |
| Tartrate of lime  | 1 |      | 260 |      | 100.00 | 100.00     | 100.000                    |

*Tartrate of Potassa and Lime* may be formed by adding lime water to solution of bitartrate of potassa, till it begins to become turbid: in a few days acicular crystals of the double salt are deposited, which effloresce when exposed to air (?)

*Tartrate of Baryta*,  $2\text{BaO}, \overline{\text{Tar}}$ , is a difficultly-soluble salt. When carefully dried it is anhydrous: it is distinguished from sulphate of baryta by its solubility in hydrochloric, nitric, and acetic acids, and by its destructibility by heat. It includes, according to Dulk, 2 atoms of water. When carbonate of baryta is boiled in water with bitartrate of potassa, a difficultly soluble white powder is obtained,  $= \text{KO}, \text{BaO}, \overline{\text{Tar}} + 2\text{HO}$ . (DULK.) Thomson has described a *bitartrate of baryta*  $= \text{BaO}, \text{HO}, \overline{\text{Tar}} + \text{HO}$ . (*First Principles*, II. 284.)

*Tartrate of Strontia*,  $2\text{SrO}, \overline{\text{Tar}} + 2\text{HO}$ , is thrown down, after some hours, on mixing the solutions of tartrate of potassa and nitrate of strontia. It dissolves in rather more than 300 parts of boiling water, and forms small rhomboidal crystals as the solution cools. (VAUQUELIN.) Thomson assigns to it the above composition.

*Tartrate of Magnesia*,  $2\text{MgO}, \overline{\text{Tar}} + 8\text{HO}$ , is precipitated from the sulphate by tartaric acid: it is soluble in excess of tartaric acid, and

forms a crystallizable *bitartrate*. When dried at  $60^{\circ}$ , it contains 8 atoms of water.

A *tartrate of potassa and magnesia*, and a *tartrate of soda and magnesia*, have been described by Dulk. (*Berzelius' Lehrbuch.*)

*Tartrate of Manganese*,  $2\text{MnO}$ ,  $\overline{\text{Tar}}$ , formed by dissolving protoxide of manganese in tartaric acid, is a soluble salt, and therefore not immediately precipitated by adding tartaric acid, or a neutral tartrate, to protochloride or protosulphate of manganese. When hot solutions of protochloride of manganese and tartrate of potassa are mixed, small crystals are deposited on cooling, which are redissolved by boiling water into a soluble supertartrate and an insoluble basic salt. (PFAFF.) When the protosalts of manganese are mixed with tartar, the oxide is not thrown down by pure or carbonated alkalis. (H. ROSE.) When tartaric acid and peroxide of manganese are boiled together in water, carbonic acid is evolved, and a colorless solution of prototartrate of manganese is obtained. Formic acid is also produced during the action of the acid and oxide. (*Quart. Journ.*, xiv. 232.)

*Tartrates of Iron*. Tartaric acid acts upon soft iron with the disengagement of hydrogen gas, and a difficultly-soluble *prototartrate of iron*, nearly white, and pulverulent, is formed. At a dull red-heat, this tartrate readily takes fire, and burns slowly away like tinder, the iron becoming peroxidized. It would probably form a valuable addition to the *Materia Medica*, having only a slight inky taste. (URE, *Quart. Journ.*, Oct., Dec., 1829.) When hot and strong solutions of tartaric acid and protosulphate of iron are mixed, white foliated crystals of *prototartrate of iron* are gradually deposited as the liquor cools. This salt contains 13 *per cent.* of water of crystallization, and is soluble in 426 parts of cold, and in 402 of boiling water. (DUMAS.) According to Dulk, this salt is anhydrous, and requires 1200 parts of water at  $60^{\circ}$  for solution.

Tartaric acid has scarcely any action upon dry sesquioxide of iron, but a *pertartrate of iron* may be obtained by mixing sesquisulphate of iron with tartrate of potassa, in equivalent proportions. Sulphate of potassa precipitates in a crystalline powder (the solutions being sufficiently concentrated), which may be separated from the blood-red liquid pertartrate of iron by filtration. Alcohol forms a treacly precipitate in this solution. When freshly precipitated and moist hydrated sesquioxide of iron is digested in an aqueous solution of tartaric acid, it is dissolved, and dries into a brown gelatinous mass; this solution is only imperfectly precipitated by caustic alkali, which throws down a basic salt, but if there be excess of the acid, there is no precipitate, and a soluble double salt is formed; so that this oxide of iron can only be precipitated from its tartaric solution by hydrosulphates, and by ferrocyanide of potassium.

*Tartrate of Potassa and Iron*. When 1 part of iron-filings and 4 of tartar are digested together with water, a greenish, astringent, and difficultly-soluble salt is formed: it is not decomposed by pure or carbonated alkalis, but by sulphuretted hydrogen. (THENARD.) By long exposure of the mixture of tartar and iron to air, or by mixing 1 part of soft iron-filings with 4 of tartar into a thin paste with water, and digesting for some weeks, till the acid is neutralized, fresh portions of water being occasionally added to prevent exsiccation, a dark-brown uncrystallizable



compound is obtained, the solution of which has been used in medicine. It is not decomposed by the alkalis. The *pertartrate of iron and potassa* is best obtained by digesting recently-precipitated hydrated sesquioxide of iron with bitartrate of potassa and water. It dissolves in alcohol. This double tartrate used formerly to be made into balls, and was employed in pharmacy under the name of *Globuli Martiales*, *Tartarus Martialis*, and *Boules de Nanci*. These were wrapped in a piece of muslin and suspended in water to form a chalybeate solution. The formula of this double tartrate is  $\text{KO}, \text{Fe}_2 \text{O}_3, \overline{\text{Tar}}$ .

*Tartrate of Zinc* is formed by adding tartrate of potassa to sulphate of zinc, and is a very difficultly soluble compound. When oxide of zinc is dissolved with tartar the solution is not affected by the alkalis, but their sulphurets throw down the whole of the zinc.

*Tartrate of Tin*. Tartrate of potassa occasions a white precipitate in the neutral protohydrochlorate and perhydrochlorate of tin. *Tartrate of potassa and tin*, formed by boiling the oxide in solution of tartar, is very soluble; the addition of alkalis and their carbonates occasions no precipitates. (THENARD, *Ann. de Chim.*, xxxviii.) A mixture of chloride of tin and tartar is used as a dyer's mordant.

*Tartrate of Cadmium*,  $2\text{CdO}, \overline{\text{Tar}}$ , is a difficultly-soluble salt, which forms acicular crystals resembling wool.

*Tartrate of Cobalt*,  $2\text{CoO}, \overline{\text{Tar}}$ , is a red crystallizable salt.

*Tartrate of Potassa and Cobalt*,  $\text{KO}, \text{CoO}, \overline{\text{Tar}}$ , forms large rhomboidal crystals. (BERZELIUS.)

*Tartrate of Nickel*.  $2\text{NiO}, \overline{\text{Tar}}$ . This salt is formed by digesting hydrated oxide, or carbonate of nickel, in a solution of tartaric acid; it is at first dissolved in the excess of acid, but afterwards falls in the form of a green crystalline powder, almost insoluble in cold and even in hot water. It is not obtained on mixing a soluble salt of the metal with a solution of tartrate of potassa, in consequence of the formation of soluble double salts. This tartrate is soluble in caustic potassa and soda, and in a hot solution of carbonated alkali, from which it expels carbonic acid; on evaporation these solutions leave a pale green mass, consisting of a double salt. When alcohol is added to the potassa solution, it throws down a gelatinous compound of hydrated oxide and tartrate of nickel. This combination is also obtained by digesting hydrated oxide of nickel in a solution of neutral tartrate of potassa, and in this case the solution does not become alkaline.

*Tartrate of Potassa and Nickel*, is formed by boiling together pulverised tartar, and carbonate of nickel in water: a green uncrystallisable and very soluble compound is formed, having the sweetness of sugar. (WERTHER. *Berzelius' Lehrbuch*.)

*Tartrate of Copper*,  $2\text{CuO}, \overline{\text{Tar}} + 6\text{HO}$ , is produced by adding tartaric acid, or a solution of tartrate of soda, to sulphate of copper. It forms a bluish-green crystalline precipitate. When dried at  $212^\circ$ , it loses about 20 per cent. of water, and becomes anhydrous. It is very sparingly soluble in water. When solutions of tartrate of soda and sulphate of copper are mixed, if they be dilute, no precipitate at first falls; but on striking the glass with a rod so as to make it vibrate, the liquor presently becomes turbid, and if lines be drawn upon the glass,

the precipitate appears upon their traces, as is the case with the ammonio-magnesian phosphate, and some other salts. This tartrate dissolves in a solution of caustic soda, forming a deep blue liquor, which is an excellent test of grape-sugar. (See SUGAR, p. 1188.)

*Tartrate of Potassa and Copper* is formed by boiling hydrated oxide of copper and tartar in water; the solution yields blue crystals on evaporation, and is used as a water color: when boiled to dryness, it furnishes one of the pigments called *Brunswick-green*.

*Tartrate of Soda and Copper*. A basic salt is obtained, according to Werthier, by precipitating a solution of tartrate of copper in caustic soda by alcohol; it falls in the form of a blue powder, which, when washed by alcohol, dissolved in water, and evaporated *in vacuo* over sulphuric acid, may be crystallized. The solution of this salt is decomposed at a boiling heat. It is represented as  $= \text{NaO}, \text{CuO}, \overline{\text{Tar}} + 2\text{CuO} + 7\text{HO}$ .

When alcohol is added to an ammoniacal solution of tartrate of copper, a blue *tartrate of ammonia and copper* falls, which is permanent in the air. (DUMENIL.)

*Tartrate of Lead*,  $2\text{PbO}, \overline{\text{Tar}} + 4\text{HO}$ , is thrown down in the form of an almost insoluble white crystalline powder, on adding tartaric acid, or a tartrate, to solution of nitrate or acetate of lead. When this tartrate is heated to a *dull-red* in a glass tube, it acquires a brown color; and, when cool, forms, as was first remarked by Dr. Göbel, a very perfect *pyrophorus*, which immediately inflames on being shaken out into the air. This property appears to depend upon the rapid oxidizement of the minutely-divided metallic lead; or, perhaps, a very oxidizable carburet of lead may be formed. According to Bötger, a powerful pyrophorus is obtained by rubbing together 4 parts of well-dried tartaric acid and  $1\frac{1}{4}$  of peroxide of lead ( $\text{Pb O}_2$ ), and heating the mixture in a phial placed in sand to dull-redness, as long as it swells up; a stopper of chalk or steatite should then be inserted, and a red-heat continued till vapors are no longer emitted: the product should then be suffered to cool, under careful exclusion of air. Tartrate of lead (anhydrous) is composed of

|                   |   |     |     |     |        | Berzelius. |       | Thomson. |        | Bucholz. |     |
|-------------------|---|-----|-----|-----|--------|------------|-------|----------|--------|----------|-----|
| Oxide of lead.... | 2 | ... | 224 | ... | 62·92  | ...        | 62·5  | ...      | 62·56  | ...      | 63  |
| Tartaric acid.... | 1 | ... | 132 | ... | 37·08  | ...        | 37·5  | ...      | 37·44  | ...      | 37  |
| <hr/>             |   |     |     |     |        |            |       |          |        |          |     |
| Tartrate of lead  | 1 |     | 356 |     | 100·00 |            | 100·0 |          | 100·00 |          | 100 |

*Tartrate of Potassa and Lead* is formed, according to Thenard, by boiling a mixture of tartar and oxide of lead in water. (*Ann. de Ch.*, xxxviii.) It is an insoluble white powder, not decomposed by the alkalis or by dilute sulphuric acid (?).

*Tartrate of Antimony*. Oxide of antimony dissolved in tartaric acid yields a very soluble, deliquescent, and difficultly-crystallizable salt,  $= 2\text{Sb O}_3 + 3 \overline{\text{Tar}}$ . When alcohol is added to the solution of this salt, a granular white precipitate falls  $= 2\text{Sb O}_3, \overline{\text{Tar}} + 2\text{HO}$ , but which is anhydrous when dried at  $212^\circ$ . (See *Berzelius' Lehrbuch*, in reference to the further properties of this salt.)

*Tartrate of Potassa and Antimony*. *Emetic Tartar*.  $\text{KO}, \text{Sb O}_3, \overline{\text{Tar}} + 2\text{HO}$ . This compound may be obtained by boiling protoxide of antimony, obtained by any of the processes formerly described, with pure



bitartrate of potassa. Emetic tartar is often prepared by boiling a mixture of equal parts of pulverised tartar and of *very finely levigated glass of antimony* in about 10 parts of water: the ebullition should be continued for half an hour, and the filtered liquor evaporated to about half its bulk, and set aside to crystallize; opaque octohedral crystals, with rhombic bases, (BROOKE, *Ann. of Phil.*, N.S., vi. 40,) of the emetic salt are thus obtained; and there is generally formed along with them a portion of tartrate of lime and potassa, which is deposited in small radiated tufts, easily separated when the mass is dried. (In reference to other modes of preparing emetic tartar, see Phillips's *Remarks on the London Pharmacopœia*; and Mohr as quoted by Soubeiran. *Journ. de Pharmacie*, Mars, 1843.)

Emetic tartar is a white salt, of a nauseous styptic taste, slightly efflorescent, soluble in about 14 parts of cold, and in less than 2 parts of boiling water. Its solution is rendered turbid by hydrochloric, nitric, and sulphuric acids, but not by the fixed alkalis: the fixed alkaline carbonates, and lime water, decompose it. Ammonia throws down oxide of antimony, especially when aided by heat. Infusion of galls and many other vegetable bitter and astringent infusions form a precipitate in solution of emetic tartar, which is generally said to be inactive, and hence decoction of bark has been recommended as an antidote to its effects. Solution of sulphuretted hydrogen only precipitates very strong solutions of emetic tartar; weaker solutions are merely reddened by it: it is also decomposed by hydrosulphuret of ammonia: in these cases the precipitate is a *golden sulphur of antimony*. Among the metals, iron only throws down the whole of the antimony. Heated to redness, out of the contact of air, it furnishes a highly-pyrophoric residue, which contains an alloy of potassium and antimony. This salt is exclusively used in pharmacy, and either sweats, vomits, or purges, according to the dose. A quarter of a grain is diaphoretic, half a grain nauseant and purgative, and one or two grains emetic; but it is given, it is said, in much larger doses, with comparative impunity, acting then chiefly as a purgative. Externally applied, as in the form of ointment, it is a powerful irritant. According to Dumas and Piria, the crystals include only 1 atom of water of crystallization; according to Wallquist 2; and according to Phillips 3; but the greater number of the analyses lead to the presence of about 5 *per cent.* of water, which indicates 2 atoms. The salt therefore may be regarded as consisting of

|                        |         |      |           |      |             | Wallquist.   | R. Phillips. |
|------------------------|---------|------|-----------|------|-------------|--------------|--------------|
| Oxide of antimony .... | 1       | .... | 153       | .... | 43.6        | .... 42.99   | .... 43.35   |
| Potassa .....          | 1       | .... | 48        | .... | 13.7        | .... 13.26   | } .... 49.25 |
| Tartaric acid.....     | 1       | .... | 132       | .... | 37.6        | .... 38.61   |              |
| Water .....            | 2       | .... | 18        | .... | 5.1         | .... 5.14    | .... 7.40    |
|                        | <hr/> 1 |      | <hr/> 351 |      | <hr/> 100.0 | <hr/> 100.00 | <hr/> 100.00 |

According to Serullas, emetic tartar is frequently contaminated by arsenious acid derived from the native sulphuret of antimony used in its preparation, so as to exhale an arsenical odor before the blowpipe.

When emetic tartar is dissolved in tartaric acid, a salt is formed, termed *neutral tartrate of potassa and antimony* =  $\text{KO}, \text{SbO}_3, 2\text{Tar} + 7\text{HO}$ : this salt is also contained in the mother-liquors of

emetic tartar. (In reference to this and other double salts of potassa and antimony, see Knapp, as quoted by Berzelius. *Lehrbuch*, iii. 1127.)

*Tartrate of Bismuth* has not been examined; but moist oxide of bismuth, boiled with tartar, forms a difficultly-soluble double salt.

*Tartrates of Uranium* are soluble, and not easily crystallizable salts. There is also a *tartrate of potassa and uranium*. (PELIGOT.)

*Tartrate of Titanium* appears to be a soluble compound; but a solution of titanate of potassa in hydrochloric acid is precipitated white by tartaric acid.

*Tartrate of Cerium*, according to Hisinger and Berzelius, is formed by adding tartrate of potassa to sulphate, nitrate, or hydrochlorate of cerium. It is a soft, tasteless powder, soluble in nitric, hydrochloric, and sulphuric acids, and in the alkalis.

*Tartrate of Tellurium* is a soluble crystallizable salt. *Tartrate of potassa and tellurium* dries into a vitreous uncrystallizable compound. (BERZELIUS.)

*Tartrate of Potassa and Arsenic*.  $\text{KO}, \text{As O}_3, \overline{\text{T}}, + 5\text{HO}$ . Pelouze has described this double tartrate, in which the oxide of antimony is apparently replaced by an equivalent of arsenic acid: 1 part of arsenic acid is dissolved in 5 of water, and the solution boiled with finely-powdered tartar: on cooling, and adding alcohol, the double salt falls in crystalline grains: it should be washed with alcohol, and dried in the air: its formula is as above given. At  $285^\circ$  it loses 5 equivalents of water. This salt is very soluble in water, but unstable, and gradually deposits tartar, arsenic acid remaining in solution; excess of arsenic acid diminishes its tendency to decomposition, and from such a solution alcohol precipitates the definite salt. (*Ann. Ch. et Ph.*, Sept. 1842.)

*Tartrate of Potassa and Molybdenum* is obtained by dissolving molybdic acid in a solution of supertartrate of potassa, and adding zinc to reduce the acid to the state of oxide: it is a difficultly-soluble salt, forming a dark-blue liquor when dissolved in ammonia. If along with the zinc a little hydrochloric acid be used, a black double salt containing protoxide of molybdenum is formed. (BERZELIUS.)

*Tartrate of Chromium*,  $2\text{Cr}_2\text{O}_3, 3\overline{\text{Tar}}$ , is obtained in the form of a blue saline mass, the solution of which is not precipitated by alkalis. Berzelius also describes a salt  $= \text{Cr}_2\text{O}_3, \overline{\text{Tar}}$ , obtained by decomposing the tartrate of lead and chromium by sulphuretted hydrogen; it forms a green uncrystallizable solution. Berlin has described two *tartrates of potassa and chromium*; one  $= \text{KO}, \text{Cr}_2\text{O}_3, \overline{\text{Tar}}$ , obtained by adding pulverized tartaric acid to a boiling solution of chromate of potassa as long as carbonic acid is evolved with effervescence, but not in excess: it is a dark green uncrystallizable compound, precipitable from its aqueous solution by alcohol. The other salt is  $3\text{KO}, \text{Cr}_2\text{O}_3, \overline{\text{Tar}}$ , obtained by adding a strong solution of neutral tartrate of potassa to the preceding salt; it forms a dark-green crystalline powder. *Tartrate of lead and chromium*,  $\text{PbO}, \text{Cr}_2\text{O}_3, \overline{\text{Tar}}$ , falls in the form of a blue-grey precipitate, on mixing solution of lead with the preceding potassa salt.

*Tartrate of Mercury*. Tartaric acid occasions white precipitates in all the solutions of the oxides of mercury, not containing excess of acid.



The tartrate of the black oxide thus obtained  $= 2\text{Hg}_2\text{O}$ ,  $\overline{\text{Tar}}$ , is crystalline and difficultly soluble. The tartrate of the red oxide  $= 2\text{HgO}$ ,  $\overline{\text{Tar}}$ , resembles the preceding in appearance.

*Tartrate of Potassa and Mercury* is formed, according to Thenard, by adding solution of tartar to nitrate of black oxide of mercury; and an analogous salt of the red oxide may be obtained by boiling it in a solution of tartar.

*Tartrate of Silver.*  $2\text{AgO}$ ,  $\overline{\text{Tar}}$ . Tartaric acid occasions no change in a dilute solution of nitrate of silver, but tartrate of potassa forms a white precipitate of tartrate of silver. Redwood recommends tartrate of silver as an ingredient in an *indelible marking ink*, which may be used without any previous application to the linen, provided, after it has been written with, the article be held to the fire, or have a hot iron passed over it, so as to develop the requisite blackness. The following are his directions:—Take of nitrate of silver 1 ounce; crystallized carbonate of soda  $1\frac{1}{2}$  ounce; tartaric acid 160 grains; strong solution of ammonia 2 ounces, or q. s; orchil  $\frac{1}{2}$  ounce, white sugar  $\frac{1}{2}$  ounce, powdered gum arabic  $1\frac{1}{2}$  ounce; distilled water q. s. (*Pharmaceutical Journ.*)

*Tartrate of Potassa and Silver.*  $\text{KO}$ ,  $\text{AgO}$ ,  $\overline{\text{Tar}}$ , is thrown down by adding tartar to nitrate of silver.

*Tartrate of Antimony and Silver.* The precipitate which falls on adding nitrate of silver to a solution of emetic tartar, consists of

|                                 |   |     |     |     |        | Wallquist. |
|---------------------------------|---|-----|-----|-----|--------|------------|
| Oxide of silver .....           | 1 | ... | 116 | ... | 27.68  | 27.31      |
| Oxide of antimony .....         | 1 | ... | 153 | ... | 36.51  | 36.94      |
| Tartaric acid .....             | 1 | ... | 132 | ... | 31.50  | 31.50      |
| Water .....                     | 2 | ... | 18  | ... | 4.31   | 4.25       |
| <hr/>                           |   |     |     |     |        |            |
| Tartrate of antimony and silver | 1 |     | 419 |     | 100.00 | 100.00     |

*Tartrate of Alumina.* This salt is very soluble, but not deliquescent; it is formed by dissolving recently-precipitated hydrate of alumina in a solution of tartaric acid, and is obtained, on evaporation, in the form of an uncrystallizable gum-like mass. It is contained in the *Lycopodium complanatum*, an infusion of which is occasionally employed as a dyer's mordant. Many wines, and especially those of Germany, contain tartrate of alumina combined with tartrate of potassa. Even neutral tartrate of potassa is capable of dissolving a considerable quantity of hydrate of alumina, and the liquor is not alkaline. The solution of tartrate of alumina is not precipitated either by caustic or carbonated alkalis. The dyer's *alumino-tartaric mordant* is made by dissolving 2 parts of tartar and 8 of alum in 8 parts of boiling water.

**ACTION OF HEAT UPON TARTARIC ACID.** The modifications which the crystallized tartaric acid undergoes under the influence of heat were first studied by Braconnot, and afterwards by Fremy, (*Ann. Ch. et Ph.*, lxxviii. 353,) who ascertained that this acid might, under especial precautions, be deprived by heat, first of *one-fourth* of its ordinary proportion of water, then of *one-half*, and *ultimately* rendered *anhydrous*. To distinguish the intermediate states of hydration between the common crystallized and the anhydrous acid, Fremy proposes for them the terms

*tartralic* and *tartrellic* acids; so that, doubling the formula of the acid for the purpose of more clearly representing these modifications, they will stand as follows:—

|                                  |                           |
|----------------------------------|---------------------------|
| Crystallized tartaric acid ..... | $C_{16} H_8 O_{20} + 4HO$ |
| Tartralic acid .....             | $C_{16} H_8 O_{20} + 3HO$ |
| Tartrellic acid .....            | $C_{16} H_8 O_{20} + 2HO$ |
| Anhydrous tartaric acid .....    | $C_{16} H_8 O_{20}$       |

In producing these modifications, small quantities of the acid, about 100 grains for instance, (a few *grammes*,) are most conveniently operated upon, in consequence of the difficulty of maintaining a given temperature throughout the mass, when a greater bulk is used.

*Tartralic Acid.* When the common acid is thus heated in a glass retort, or porcelain capsule placed in an oil-bath, up to  $392^{\circ}$  ( $200^{\circ}$  Cent.), so as to fuse but not discolor it, it acquires a viscid consistence, is deliquescent, uncrystallizable, and soluble in alcohol. In this state it is *tartralic acid*, having lost *one-fourth* of its water, and acquired distinct properties; but if it be re-dissolved in water, it resumes in the course of 24 hours (or *immediately*, if boiled) its former characters, and may then be crystallized as usual. The cold aqueous solution of tartralic acid, used immediately after it is prepared, forms *soluble salts with lime and baryta*, whereas the ordinary acid yields difficultly soluble salts with those bases; so that any portion of unchanged tartaric acid may be separated from the tartralic, by the addition of carbonate of lime or baryta to the solution in cold water, and filtration. When alcohol is then added to the filtered liquor, it throws down the earthy *tartrate* in the form of a viscid substance, which may be dried over oil of vitriol *in vacuo*, and then remains unchanged. If a solution of this baryta-salt be immediately decomposed by sulphuric acid, filtered, and evaporated *in vacuo*, the tartralic acid is again obtained with all its peculiarities; but if too much water is used, and the evaporation protracted, even without the application of heat, either the common acid, or a mixture of it with the modified acid, is the result. If a solution of one of the preceding salts be boiled, it becomes sour in consequence of the resumption of water by the partially dehydrated acid, and common tartrate of lime or of baryta is precipitated. The *alkaline tartrates* are with difficulty obtained, in consequence of the tendency of the tartralic acid to revert to the ordinary acid when in solution with an alkali. On analyzing *tartrate of lime*, and *tartrate of baryta*, Fremy found them to consist of 3 atoms of basis combined with 2 of acid, so that the *tartrate of lime* would be  $= 3CaO, + C_{16} H_8 O_{20}$ ; and in the conversion of tartrate of lime into free tartaric acid and common tartrate of lime, 2 atoms of the *tartrate*, acted upon by water, are transformed into 3 atoms of tartrate, 1 of tartaric acid, and 4 of water:  $2[3CaO, C_{16} H_8 O_{20} + 2HO] = 3[2CaO, C_8 H_4 O_{10}] + C_8 H_4 O_{10} + 4HO$ .

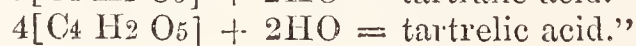
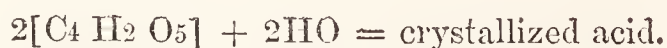
*Tartrellic Acid* is obtained by first heating the tartaric acid as in the preceding case, to  $392^{\circ}$ , then lowering the temperature to  $356^{\circ}$ , and keeping it for some time at that point, when it loses half its original water, and becomes  $= C_{16} H_8 O_{20} + 2HO$ . This acid resembles the tartralic in appearance, but is slightly yellow; it is deliquescent, and the *tartrelates of lime* and of *baryta* have the general character of the corre-



sponding tartralates. This acid passes into tartaric acid, and its salts are converted into tartrates and free tartaric acid, in the same way as the preceding.

When tartrelic acid is kept at  $356^{\circ}$ , beyond the time required for its formation, and after it has begun to assume a yellow tint, it continues to lose water, and passing through a state of hydration  $= C_{16} H_8 O_{20} + HO$ , it at length becomes brown and anhydrous.

*Anhydrous tartaric acid* may be obtained colorless, by heating about 300 grains of pulverized tartaric acid in a porcelain capsule over a small charcoal fire; it first fuses, and then rapidly passes through the preceding states of hydration, and swells up into a white porous anhydrous mass; it is then taken out of the capsule, and kept for a short time in an oil-bath, heated to about  $300^{\circ}$ . If this precaution be not taken, it is apt to *gelatinize* when put into water, and in that state, the remains of any undecomposed common, or hydrated acid, cannot easily be washed out of it; whereas, after having been heated as described, it may be washed with ice-cold water as long as anything soluble is removed, and then rapidly dried *in vacuo* over sulphuric acid. It is then a white amorphous substance, at first tasteless, but after a time impressing a sourness upon the tongue. It is in the first instance insoluble in *cold* water, in alcohol, and in ether, but the protracted action of water gradually converts it into the ordinary hydrated acid, and if boiled, the change is almost immediately effected. In a solution of potassa it yields common tartrate of potassa. "It would appear," says Dr. Gregory, speaking of the conversion of the preceding acids into tartaric acid by boiling in water, "as if in the tartralic and tartrelic acids an additional quantity of anhydrous acid had been added to the radical, without affecting the neutralizing power; just as in phosphoric, pyrophosphoric, and metaphosphoric acids. If *anhydrous tartaric acid* be represented as  $C_4 H_2 O_5$ , then



XIII. PYROTARTARIC ACID. This acid was discovered by Gehlen in 1806 (*Ann. de Chim.*, LX. 79); its properties and preparation were afterwards more fully inquired into by Fourcroy and Vauquelin, (*Ibid.*, LXIV. 42). Valentin, Rose, Weniselos, Pelouze, and Liebig, are the latest authorities upon it. (BERZELIUS, *Lehrbuch*.) It is very sparingly produced during the destructive distillation of tartaric acid, but is more abundantly obtained from *tartar*, according to the following directions of Weniselos. A tubulated retort, to which a tubulated receiver is attached, is two-thirds filled with bitartrate of potassa, and is gradually heated in a sand-bath; watery vapor, acetic acid, and carburetted hydrogen gas are at first evolved, and then, drops of a sour brown liquid, and an oily product. The operation is continued as long as a liquid distils, and when this ceases, the receiver is removed, and its contents poured upon a filter, by which the aqueous and the oily products are separated, the aqueous part is brown, and has a slightly acid reaction, and a pungent taste; it is evaporated upon a water-bath, by which acetic acid is driven off, and when small crystals begin to form, it should be removed, and left to

spontaneous evaporation, if possible by exposure to the sun, when the pyrotartaric acid slowly separates in small granular crystals, which must be purified by repeated solution and crystallization. The brown acid which remains in the mother-liquor may be purified by heating it with a little fuming nitric acid, which decomposes the empyreumatic oil, but does not affect the pyrotartaric acid. The nitric acid may be expelled by heat, and the residue dissolved in water and crystallized.

The concentrated aqueous solution of pyrotartaric acid, when slowly cooled, deposits rhombic prisms; but if evaporated, the acid remains in a white amorphous mass, inodorous, and very sour. It fuses at a little above  $212^{\circ}$ , then boils, and evaporating at about  $320^{\circ}$ , crystallizes in the receiver. It is soluble in about 3 parts of water; it also dissolves in alcohol and in ether. The crystallized acid is *hydrated*; anhydrous pyrotartaric acid not having been separately obtained. Its formula is  $C_5 H_3 O_3 + HO$ . It may result from the abstraction of 3 atoms of carbonic acid and 1 of water from 1 atom of anhydrous tartaric acid. Thus  $C_8 H_4 O_{10} - 3CO_2, HO = C_5 H_3 O_3$ .

The *pyrotartrates*,  $=MO, C_5 H_3 O_3$ , are almost all very soluble; the neutral compounds are mostly uncrystallizable, but with many bases it forms crystallizable acid salts, several of which have been described by V. Rose, Weniselos, and Gruner. (See *Berzelius' Lehrbuch*, iv. 236.)

**XIV. PYRUVIC ACID. *Pyroracemic Acid. Liquid Pyrotartaric Acid.*** This acid was discovered by Berzelius in 1834, during a series of comparative experiments on the tartaric and racemic acid; its production had been previously observed by Pelouze, who, regarding it as acetic acid, did not further examine it. It is produced during the dry distillation both of tartaric and of racemic acid. The acid is introduced into a tubulated retort, to which a tubulated receiver is adapted, and placed in a sand heat; it fuses, boils up, and becomes yellow, brown, and ultimately black, but care should be taken that the temperature does not at any time exceed  $390^{\circ}$  to  $400^{\circ}$ . The boiling over of the acid must be prevented by occasionally stirring it through the tubulature with a stiff wire, and this must be done frequently, so as to keep it down in the retort. At first a colorless acetous liquid goes over; then carbonic acid is evolved, carrying with it acetic and pyrotartaric vapor; the distillate gradually acquires a yellow tint, but never gets brown if caution be observed to keep down the temperature of the retort below  $428^{\circ}$ , the contents of which blacken, but lose viscosity and boil quietly; and when, at the temperature of  $428^{\circ}$ , nothing further distils, the operation is ended. The residue in the retort is hard, carbonaceous, and porous, when cold; it is insoluble in water, somewhat soluble in alcohol, and more so in carbonated alkalis; it contains various substances belonging to the class of weak acids, which have not been minutely examined.

The distilled acid is pungent and sour, and has an acetous empyreumatic odor; the specific gravity of the last distilled portions is sometimes as high as 1.28; it contains several substances, the more volatile of which may be separated by distillation in a water-bath, and consist chiefly of pyruvic and acetic acid. This product is then saturated by recently precipitated and moist carbonate of lead, which is at first dissolved, but after a time an abundant granular deposit of the lead salt



ensues: the carbonate of lead is added as long as carbonic acid is expelled, but heat must not be applied, as it would affect the pyruvic acid. As the whole of the lead salt is not immediately precipitated, the mixture is left for 24 hours in a cold place, and the precipitate then washed upon a filter with a little cold water, in which the salt is but sparingly soluble. The mother liquor which runs off may be evaporated spontaneously, or in vacuo over sulphuric acid, when acetic acid escapes, and a portion of gum-like pyruvate remains. The pyruvate of lead is then mixed with a little water, decomposed by sulphuretted hydrogen, and the resulting acid solution evaporated in vacuo over sulphuric acid. It is at first colorless, but acquires a yellow tint during the evaporation.

Pyruvic acid thus obtained is of a thick consistence, uncrystallizable, inodorous when cold, but of a pungent acid odor when heated. It tastes sour, and afterwards bitterish. It mixes in all proportions with water, alcohol, and ether. In this state it is a *hydrated acid*, the formula of which is  $C_6H_3O_5 + HO$ ; it results from the abstraction of 2 atoms of carbonic acid and 1 of water, from 1 of anhydrous tartaric acid. Thus,  $C_8H_4O_{10} - 2CO_2, HO = C_6H_3O_5$ .

*Pyruvates.* Many of these salts may be crystallized, but the acid is so easily decomposed by heat, even when it is in combination with the stronger bases, that on saturating it, it must not be used in too concentrated a state, as it then becomes yellow or brown. The pyruvates exist under two modifications, *crystalline*, and *amorphous* or *gum-like*. The former are obtained when heat is excluded, and are most perfect when formed at the lowest temperatures. The latter are produced by boiling the dilute saline solution, and then evaporating it. In some cases, as with the salts of the alkaline earths, the gummy condition is induced by a gentle heat, and the salt cannot revert to the crystalline modification. A concentrated boiling solution of the crystalline salts generally again crystallizes on cooling; so that effectually to induce the gummy state, the salt must be boiled in *dilute* solution. The dry salts, in either condition, are easily rendered yellow by heat; many of them at  $212^\circ$ , and all of them at  $250^\circ$ . In these cases they first acquire a lemon yellow, and then an orange color, as is more especially the case with the hydrated acid itself. The dry pyruvates are decomposed by sulphuric acid, but the pyruvic acid cannot thus be obtained without decomposition. The greater number of the pyruvates are soluble in caustic and carbonated alkalis; they are very sparingly soluble in absolute alcohol, and insoluble in ether. They are recognized, when in solution, by dropping in a solution of protosulphate of iron, or a fragment of a crystal of that salt, when they become deep red. A fragment of sulphate of copper produces, after some hours, a nearly white precipitate, provided the solution of the pyruvate is not too dilute.

Pyruvic acid expels acetic acid from the acetates, and precipitates the bases of those soluble acetates with which it forms difficultly soluble combinations. Its salts, when dried, are colorless, transparent, and gum-like, and redden litmus. Many, when neutral, are insoluble, and are decomposed by water; others by alcohol; and others, as for example the alkaline salts, are only deprived by alcohol of a portion of their acid. (BERZELIUS, *Lehrbuch*, iv. 221, where will be found a detailed account of this acid, and of its salts.)

XV. RACEMIC ACID.  $\overline{\text{Rc}}$ . *Uvic Acid*. *Paratartaric Acid*. This curious modification of the tartaric acid was discovered by Kestner, a manufacturer of tartaric acid, at Thann, a small town in Wasgau (*Département du haut Rhin*); he appears to have mistaken it for oxalic acid; but in 1819 John observed its peculiarities (*Handwörterbuch der Chemie*, iv. 125): and in 1826, Gay Lussac and Walchner examined it, and shewed it to be a distinct acid. In 1830 Berzelius demonstrated the identity of composition of this acid and the tartaric, thus giving the first example of *isomerism* in organic bodies, (*Annalen der Physik*, xix. 305; *Ann. Ch. et Ph.*, lxvi. 128.) This acid was at first considered as peculiar to the grapes of the district in which it was originally discovered (and was therefore distinguished as *Acide des Vosges*), but it probably exists very generally in the juice of sour grapes.

Racemic acid is obtained by saturating the tartar of sour grapes, more especially the tartar obtained from the grapes grown in the above-mentioned district, with carbonate of soda, and allowing the double tartrate of potassa and soda to crystallize; the double racemate being more difficult of crystallisation, remains in the mother-liquor, which, after having been decolored by filtration through animal charcoal, is precipitated by a salt of lime or lead, and the precipitate decomposed either by sulphuric acid or by sulphuretted hydrogen. The solution thus obtained contains both racemic and tartaric acid; on evaporating it, the racemic acid crystallizes first; the tartaric acid not crystallizing till the liquor begins to acquire a syrupy consistence.

The crystals of racemic, closely resemble those of tartaric acid, but the former are oblique prisms with a rhombic base, while the latter are oblique prisms with a rectangular base; but when the crystals are not sufficiently distinct for the observation of their forms, they may be distinguished by heating them, when the tartaric crystals acquire electropolarity, which is not the case with the racemic.

Racemic acid may be obtained *anhydrous* in the same way as the tartaric, and in this state, as also in the intermediate condition of hydration, it so exactly resembles the tartaric acid, that it might have been supposed to have passed into it; but when redissolved, and allowed to resume its water, racemic, and not tartaric acid, is the result. The *anhydrous* racemic acid, the equivalent of which is 66, =  $\overline{\text{Rc}}$ , consists of

|                              |   |     |    |     |        |
|------------------------------|---|-----|----|-----|--------|
| Carbon .....                 | 4 | ... | 24 | ... | 36·37  |
| Hydrogen .....               | 2 | ... | 2  | ... | 3·03   |
| Oxygen .....                 | 5 | ... | 40 | ... | 60·60  |
| <hr/>                        |   |     |    |     |        |
| Anhydrous racemic acid ..... | 1 |     | 66 |     | 100·00 |

The acid dried at  $212^{\circ}$ , is  $\text{HO}, \text{C}_4 \text{H}_2 \text{O}_5$ , =  $[\text{HO}, \overline{\text{Rc}}]$ , its equivalent being  $66 + 9 = 75$ ; and the crystallized acid being  $\text{HO}, \text{C}_4 \text{H}_2 \text{O}_5 + \text{HO} = [\text{HO}, \overline{\text{Rc}} + \text{HO}]$ , has the equivalent  $75 + 9 = 84$ . The acid dried at  $212^{\circ}$ , contains therefore 12 *per cent.* of basic or constitutional water, while the ordinary crystallised acid contains 10·7 *per cent.* of water of crystallization, or 21·4 *per cent.* of water, including both. When the crystallised acid is left in a warm place it becomes opaque but does not fall into powder, losing *water of crystallization*, the whole of which may be expelled at  $212^{\circ}$ . The remaining porous acid, which still retains



the form of the hydrated crystals, does not begin to part with its *basic water* till heated to  $392^{\circ}$ .

Crystallised racemic acid is soluble in somewhat less than 6 parts of water at  $60^{\circ}$ , but much more soluble in boiling water. It is less soluble in alcohol than in water, but very soluble in ether.

*Racemates.* These salts, which have been especially studied by Fresenius (*Ann. der Chem. und Pharm.*), closely resemble the tartrates. Racemate of lime is less soluble than sulphate of lime, whereas tartrate of lime is about of the same degree of solubility; so that a saturated aqueous solution of sulphate of lime is not precipitated by tartaric acid, but it is precipitated, at least after a short time, by a solution of racemic acid. This acid may also be precipitated from its salts by chloride of calcium, and if the precipitate be dissolved in dilute hydrochloric acid, and mixed with caustic ammonia, a white precipitate of racemate of lime immediately forms, but is long in subsiding. A tartrate treated in the same way affords no immediate precipitate, although after a time the glass becomes lined with minute crystals of tartrate of lime.

Racemic acid forms *neutral salts*,  $= \text{MO}, \overline{\text{Rc}}$ , and *acid salts*,  $= \text{MO}, \overline{\text{Re}} + \text{HO}, \overline{\text{Rc}}$ ; thus the *neutral racemate of potassa* is  $\text{KO}, \overline{\text{Rc}} + 2\text{HO}$ ; and the *acid racemate of potassa* is  $\text{KO}, \overline{\text{Rc}} + \text{HO}, \overline{\text{Re}}$ ; so that these salts correspond to the two tartrates. "Were it not that we must admit tartaric acid to be *bibasic*, we should find it difficult to account for the differences which exist between the two acids. We have here a very near approach to the occurrence of different properties with the same composition, and even the same arrangement. The two acid salts of potassa, for example, are  $\text{C}_8 \text{H}_4 \text{O}_{10} \left\{ \begin{array}{l} \text{KO}, \\ \text{HO}, \end{array} \right.$  for the *bitartrate*; and  $\text{C}_4 \text{H}_2 \text{O}_5, \text{KO}, + \text{C}_4 \text{H}_2 \text{O}_5, \text{HO},$  for the *biracemate*. If we represent the latter as follows,  $\text{C}_4 \text{H}_2 \text{O}_5 \left\{ \begin{array}{l} \text{KO}, \\ \text{C}_4 \text{H}_2 \text{O}_5 \left\{ \begin{array}{l} \text{HO}, \end{array} \right. \end{array} \right.$  we see how very nearly alike they are, even on the view we have adopted of the one acid being *bibasic*, and the other *monobasic*; and we must bear in mind that these two salts are strikingly similar in properties. The same remarks apply to the crystallized acids, and to the double salts with antimony; although in the case of the two acids, we have evidence of one point of difference in the arrangement. Tartaric acid is  $\text{C}_8 \text{H}_4 \text{O}_{10}, 2\text{HO}$ , while racemic acid is  $\text{C}_4 \text{H}_2 \text{O}_5, \text{HO} + \text{aq.}$ , and loses the water of crystallization at  $212^{\circ}$ ." (GREGORY, *Outlines*, 414.)

*Racemate of Ammonia*,  $\text{NH}_4 \text{O}, \overline{\text{Rc}}$ , forms efflorescent prismatic crystals, easily soluble in water, and containing no water of crystallization.

*Biracemate of Ammonia*,  $\text{NH}_4 \text{O}, \overline{\text{Rc}} + \text{HO}, \overline{\text{Re}}$ , forms a crystalline precipitate, requiring 100 parts of water at  $68^{\circ}$  for solution: it only contains the atom of basic water belonging to the acid.

*Racemate of Potassa*,  $\text{KO}, \overline{\text{Rc}}$ , forms hard transparent but irregular 4-sided prisms, which effloresce at  $212^{\circ}$ , and lose 13.7 per cent. of water. This salt is soluble in 0.97 parts of water at  $78^{\circ}$ , but almost insoluble in alcohol.

*Biracemate of Potassa*,  $\text{KO}, \overline{\text{Rc}} + \text{HO}, \overline{\text{Re}}$ , crystallizes out of a saturated boiling solution, in small 4-sided tables; or it may be thrown down in the form of a crystalline powder: it is soluble in 180 parts of water at  $65^{\circ}$ , in 139 parts at  $76^{\circ}$ , and in 14.3 parts at  $212^{\circ}$ . It is insoluble in alcohol.

*Racemate of Soda*,  $\text{NaO}, \overline{\text{Rc}}$ , forms transparent 4-sided rhombic prisms, anhydrous, soluble in 2·6 parts of water at  $68^\circ$ , and insoluble in alcohol.

*Biracemate of Soda*,  $\text{NaO}, \overline{\text{Rc}} + \text{HO}, \overline{\text{Rc}}$ , forms small brilliant striated crystals, containing 2 atoms of water of crystallization, which it loses at  $212^\circ$ . It is soluble in 11·3 parts of water at  $65^\circ$ , and insoluble in alcohol.

*Racemate of Potassa and Soda*,  $\text{KO}, \overline{\text{Rc}} + \text{NaO}, \overline{\text{Rc}}$ , is obtained either by dissolving atomic weights of the salts, or by saturating the biracemate of potassa with soda. By spontaneous evaporation it forms large hard transparent rhombic tables or prisms, containing 8 atoms = 25·5 per cent. of water of crystallization, which they lose when dried at  $212^\circ$ . This is the same number of atoms of water as is contained in the corresponding tartrate (Rochelle salt), but the two salts are not isomorphous. This salt is very soluble in water (in all proportions in boiling water.) At  $212^\circ$  it loses its water of crystallization without fusing. If crystallized below  $45^\circ$ , only 6 atoms of water of crystallization are consolidated, but the form is the same as with 8 atoms.

*Racemate of Lime*,  $\text{CaO}, \overline{\text{Rc}}$ , forms brilliant acicular crystals, containing 24·5 per cent. of water of crystallization: when precipitated from concentrated solutions, by double affinity, it is a white powder.

*Racemate of Baryta*,  $\text{BaO}, \overline{\text{Rc}}$ . When racemic acid is added to a solution of acetate of baryta, it gradually forms a mass of acicular crystals almost insoluble in water and in acetic acid. If this salt be precipitated at a boiling heat, it forms a white anhydrous crystalline powder, more soluble in racemic acid than in water, but forming no acid salt: nor does it form double salts.

*Racemate of Magnesia*,  $\text{MgO}, \overline{\text{Rc}}$ , forms small rhombic prisms, when carbonate of magnesia is dissolved in a boiling solution of racemic acid, and suffered slowly to cool.

*Racemate of Protoxide of Iron*,  $\text{FeO}, \overline{\text{Rc}}$ , falls, by double decomposition, as a white precipitate, becoming yellow, green, and brown, when exposed to air. It is very little soluble in water, but readily soluble in acids and in alkalis. Its acid solutions are not precipitated by alkalis, nor are its alkaline solutions precipitated by acids.

*Racemate of Peroxide of Iron*,  $\text{Fe}_2\text{O}_3, 3\overline{\text{Rc}}$ , obtained by digesting hydrated peroxide of iron in a solution of the acid, and filtering from the basic salt at the same time formed, is a brown solution, which leaves a brown amorphous mass on evaporation, soluble in water, and not precipitated by alkalis. It forms a deliquescent double salt with racemate of potassa. The basic salt is a yellow powder, soluble in racemic acid and in solution of potassa.

*Racemate of Lead*,  $\text{PbO}, \overline{\text{Rc}}$ , is obtained crystalline, when a solution of racemic acid is dropped into a hot solution of acetate of lead as long as the precipitate is re-dissolved. On cooling, the salt forms granular and acicular crystals, which decrepitate and fall to powder when heated, but contain no water of crystallization.

*Racemate of Copper*,  $\text{CuO}, \overline{\text{Rc}}$ , is deposited during the evaporation of a mixed solution of acetate of copper and racemic acid, in small pale



blue 4-sided prisms, sparingly soluble in water. This salt is also precipitated in the form of a green powder, by double decomposition. A hydrated compound of racemate of soda with oxide of copper is obtained by dissolving the racemate of copper in caustic soda to saturation, and precipitating by alcohol; it is  $\text{NaO}, \overline{\text{Rc}} + \text{CuO}, \text{HO}, + 3\text{HO}$ . When the soda-solution is in excess, octohedral crystals are formed  $= 3\text{NaO}, \overline{\text{Rc}} + \text{CuO}, \text{HO}$ .

*Racemate of Potassa and Antimony*,  $\text{KO } \overline{\text{Rc}} + \text{SbO}_3, \overline{\text{Rc}}$ , is formed by saturating a boiling solution of biracemate of potassa with oxide of antimony; on cooling, the salt is deposited in 4-sided prisms with rhombic bases, containing 2 atoms of water of crystallization. When heated to  $320^\circ$ , this salt suffers a decomposition similar to that sustained by emetic tartar.

*Racemate of Silver*,  $\text{AgO}, \overline{\text{Rc}}$ , forms a white precipitate which blackens by exposure to light: it contains 1 atom of water. Dissolved in ammonia, and evaporated on the sand-heat, it deposits metallic silver.

XVI. CITRIC ACID.  $\text{C}_{12} \text{H}_5 \text{O}_{11} = \overline{\text{Ci}}$ . This acid, which was discovered by Scheele, (*De succo citri. Opusc.*, ii., 181,) in 1784, exists in many vegetables; it is especially abundant in *lemon* and in *lime-juice*; it is also contained in currants, gooseberries, raspberries, and strawberries, in the berries of *vaccinium*, and in the onion and potato. It is mostly in a free state, or in the form of acid salts.

Citric acid is obtained from lemon and lime-juice as follows, the juice being sometimes submitted to an incipient fermentation, in order to separate mucilage, which is then deposited, and the clear liquor afterwards poured off for use; or in other cases the juice is heated, and clarified by white of egg: it is then saturated, at a temperature approaching its boiling point, with finely-powdered chalk, which is added in small portions at a time, as long as effervescence ensues, 16 parts of the juice generally requiring about 1 part of chalk. In consequence of the formation of an acid salt of lime, the effervescence ceases before the whole of the acid is precipitated, in order to effect which, small portions of hydrate of lime may be added, till the liquor no longer reddens litmus; it is then allowed to cool, and the precipitated citrate of lime separated upon a strainer, and well washed and stirred up with hot water, till the strained liquor runs off clear and colorless. The citrate is then decomposed by stirring it into a warm mixture of 1 part of oil of vitriol and 6 of water, the quantity of oil of vitriol required being about equal in weight to that of the chalk used in saturating the juice. In this part of the process care must be taken gradually to mix the acid and citrate under constant stirring, otherwise it is apt to get lumpy, and occasion much trouble in subsequently diffusing it. This mixture, being occasionally stirred, is left for some hours till the decomposition of the citrate is complete; the clear liquor is then decanted from the deposited sulphate of lime, which is washed with a little cold water. The citric solution is then boiled down till it acquires the sp. gr. 1.13, after which, the evaporation must be carefully continued, by steam heat, or in a water-bath, to the consistency of thin syrup; and as soon as a crystalline pellicle or crust appears on its surface, the heat must be withdrawn, for if evaporated beyond that point, the citric acid blackens. In about four days the mother-liquor is

poured off the crop of crystals, and evaporated with the same precautions as before, and this is repeated till clean crystals can no longer be obtained; the remaining liquor is then diluted, and treated in the same way as the original lemon-juice. Two or three solutions and crystallizations are required to obtain the acid pure and colorless. The addition of a little alcohol to the liquor sometimes facilitates the formation of the crystals.

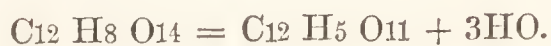
The preparation of this acid is carried on by a few manufacturers upon an extensive scale; in different states of purity, it is employed by calico-printers, and used in pharmacy, and for domestic consumption. Some circumstances which have not been above alluded to, but which are said to contribute to the success of the process, have been described by Parkes, in the third volume of his *Chemical Essays*. The average proportion of citric acid afforded by a gallon of good lemon-juice, is about 8 ounces; but Dr. Henry states that he has occasionally obtained as much as 12 ounces.

M. Tilloy, of Dijon, recommends *currants* as a source of citric acid: they are bruised, and the expressed juice is fermented, and then distilled to obtain the alcohol: the residue is saturated by chalk, and the washed citrate of lime decomposed by sulphuric acid: from 100 parts of currants he obtained 10 of alcohol and 1 of acid. (*Ann. de Ch. et Ph.*, xxxix. 222.)

Citric acid is sometimes fraudulently mixed with tartaric acid: the adulteration may be discovered by adding to the acid dissolved in cold water, a solution of acetate of potassa, which will occasion the precipitation of bitartrate of potassa, if tartaric acid be present. When citric acid is added to lime-water, the liquid remains clear till it is heated, and then becomes turbid and deposits citrate of lime. This character distinguishes citric acid from most of the other vegetable acids.

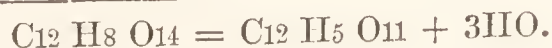
When 1 part of crystallized citric acid is gently heated with 4 parts of oil of vitriol, carbonic oxide and carbonic acid are evolved, and if water be then added and the mixture distilled, acetic acid passes over; 1 atom of the terhydrated citric acid, containing the elements of 2 atoms of carbonic acid, 2 of carbonic oxide, 2 of acetic acid, and 2 of water.

|                               |         |     |
|-------------------------------|---------|-----|
| 2 atoms of carbonic acid..... | C 2     | O 4 |
| 2 „ carbonic oxide .....      | C 2     | O 2 |
| 2 „ acetic acid.....          | C 8 H 6 | O 6 |
| 2 „ water.....                | H 2     | O 2 |



When citric acid is decomposed by fusion with caustic potassa, it yields 2 atoms of oxalic acid, 2 of acetic acid, and 2 of water.

|                             |         |     |
|-----------------------------|---------|-----|
| 2 atoms of oxalic acid..... | C 4     | O 6 |
| 2 „ acetic acid.....        | C 8 H 6 | O 6 |
| 2 „ water.....              | H 2     | O 2 |



When a solution of citric acid is heated with peroxide of manganese, carbonic acid and acetic acid are formed: with red oxide of mercury it produces effervescence, and a white salt, containing, according to Vau-



quelin, acetic acid. When citric acid is heated with chloride of gold, it reduces it without any evolution of gas. (LIEBIG.)

Citric acid forms beautiful crystals, of which the primary form is a right rhombic prism. They have a very sour taste, and are soluble in somewhat less than their own weight of water at  $60^{\circ}$ , and in half their weight at  $212^{\circ}$ . They also dissolve in alcohol, but not in ether. Their diluted aqueous solution soon becomes mouldy.

Citric acid is *tribasic*, and may be represented as  $= \text{C}_{12} \text{H}_5 \text{O}_{11}, 3\text{HO}$ ; or  $\overline{\text{Ci}}, 3\text{HO}$ . The *ordinary* crystals of citric acid deposited from its hot saturated solution, contain 1 additional atom of water, and are therefore  $= \overline{\text{Ci}}, 3\text{HO} + \text{HO}$ , or  $\overline{\text{Ci}}, 4\text{HO}$ ; but the crystals deposited by *spontaneous evaporation* from a cold solution, contain 2 additional atoms of water, and are  $\overline{\text{Ci}}, 3\text{HO} + 2\text{HO}$ , or  $\overline{\text{Ci}}, 5\text{HO}$ . The ordinary crystals, just mentioned as being  $= \overline{\text{Ci}}, 4\text{HO}$ , neither lose weight nor transparency when exposed to a temperature of  $212^{\circ}$ ; but the crystals from the cold solution, and which are  $= \overline{\text{Ci}}, 5\text{HO}$ , lose under the same circumstances 2 atoms of water, and become  $\overline{\text{Ci}}, 3\text{HO}$ . Both of these crystalline modifications enter into fusion at  $256^{\circ}$ , and when heated above  $300^{\circ}$ , are decomposed with results afterwards to be noticed. It appears, therefore, that the *anhydrous citric acid*, which has not been isolated, as it exists for instance in citrate of silver, is constituted of

|                            |    |     |     |     |        |
|----------------------------|----|-----|-----|-----|--------|
| Carbon .....               | 12 | ... | 72  | ... | 43.64  |
| Hydrogen .....             | 5  | ... | 5   | ... | 3.03   |
| Oxygen .....               | 11 | ... | 88  | ... | 53.33  |
| <hr/>                      |    |     |     |     |        |
| Anhydrous citric acid..... | 1  |     | 165 |     | 100.00 |

The acid obtained by subjecting the crystals deposited by a saturated cold solution, to a temperature of  $212^{\circ}$ , contains

|   |   |     |     |     |        |
|---|---|-----|-----|-----|--------|
| Anhydrous citric acid .....                           | 1 | ... | 165 | ... | 85.94  |
| Water .....   | 3 | ... | 27  | ... | 14.06  |
| <hr/>   |   |     |     |     |        |
| Crystals of cold solution dried at $212^{\circ}$ .... | 1 |     | 192 |     | 100.00 |

The ordinary crystals of the acid, which are deposited from its hot saturated solution, contain

|  |   |     |     |     |        |
|--|---|-----|-----|-----|--------|
| Anhydrous acid .....                   | 1 | ... | 165 | ... | 82.09  |
| Water .....                            | 4 | ... | 36  | ... | 17.91  |
| <hr/>                                  |   |     |     |     |        |
| Ordinary crystallized citric acid..... | 1 |     | 201 |     | 100.00 |

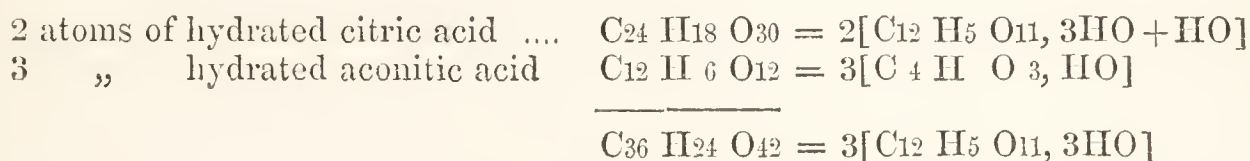
The crystals as deposited by spontaneous evaporation from a cold saturated solution, contain

|                                |   |     |     |     |        |
|--------------------------------|---|-----|-----|-----|--------|
| Anhydrous acid .....           | 1 | ... | 165 | ... | 78.57  |
| Water .....                    | 5 | ... | 45  | ... | 21.43  |
| <hr/>                          |   |     |     |     |        |
| Crystals of cold solution..... | 1 |     | 210 |     | 100.00 |

(In reference to these results, see BERZELIUS, *Ann. Ch. et Ph.*, lii. 424 and 432; and LIEBIG, *ibid.* 430 and 434. Also LIEBIG, *Traité de Chim. Org.*, ii. 36; and BERZELIUS, *Lehrbuch*, iv. 136. Edit. 1846.)

*Citrates.* Citric acid forms three classes of salts, containing respectively; 3 atoms of fixed base; 2 atoms of fixed base and 1 of water; and 1 atom of fixed base and 2 of water; in these respects resembling the phosphoric acid, in which the water of crystallization of the crystallized acid is replaced by a fixed base. Thus, we have salts  $= 3\text{MO}, \overline{\text{Ci}}$ ;  $2\text{MO}, \text{HO}, \overline{\text{Ci}}$ ; and  $\text{MO}, 2\text{HO}, \overline{\text{Ci}}$ . The *basic salts*, corresponding to the two forms of the crystallized acid, are  $3\text{MO}, \overline{\text{Ci}} + \text{MO}$ ; and  $3\text{MO}, \overline{\text{Ci}} + \text{MO}, \text{HO}$ .

When a dry citrate with 3 atoms of base ( $= 3\text{MO}, \overline{\text{Ci}}$ ) is decomposed by an alcoholic solution of gaseous hydrochloric acid, so that no more water is presented to the evolved citric acid than the 3 atoms derived from the oxygen of the base and the hydrogen of the hydrochloric acid, there are formed, from the 3 atoms of dry citric acid, 2 atoms of hydrated citric acid with 1 atom of water of crystallization, and 3 atoms of *hydrated aconitic acid*; this change, resembling that which ensues on heating citric acid up to a certain point, will presently be noticed more in detail; it is as follows:



None of the citrates endure a temperature of  $450^\circ$  without decomposition, and many of them are discolored even before they attain that temperature. These salts have been especially studied by Heldt, an abstract of whose researches is given by Berzelius. (*Lehrbuch*, iv. 140.)

*Citrate of Ammonia.* The neutral salt,  $3\text{NH}_4 \text{O}, \overline{\text{Ci}}$ , has not been obtained in a solid form, for it loses ammonia on evaporation. When an alcoholic solution of citric acid is saturated by ammonia, the neutral citrate separates in the form of a concentrated aqueous solution. The salt resulting from the evaporation of the neutral citrate, forms prismatic crystals, which are  $= 2\text{NH}_4 \text{O}, \text{HO}, \overline{\text{Ci}}$ . A crystallizable salt  $= \text{NH}_4 \text{O}, 2\text{HO}, \overline{\text{Ci}}$ , may also be obtained.

*Citrate of Potassa.*  $3\text{KO}, \overline{\text{Ci}}$ . This salt is much used in medicine as a mild diaphoretic; it is the *Salt of Riverius*, of old pharmacy. When evaporated, first by heat and then spontaneously, it forms stellated groups of acicular crystals; it is deliquescent, and very soluble in water, but insoluble in alcohol, which separates it from water in the form of a concentrated aqueous solution. There is also a citrate of potassa  $= 2\text{KO}, \text{HO}, \overline{\text{Ci}}$ , which is uncrystallizable; and a third  $= \text{KO}, 2\text{HO}, \overline{\text{Ci}}$ , which forms prismatic crystals.

*Citrate of Soda.*  $3\text{NaO}, \overline{\text{Ci}}, + 11\text{HO}$ . This salt crystallizes from its concentrated aqueous solution in large regular crystals, which effloresce in a dry and warm atmosphere. At  $212^\circ$  it loses 17.5 per cent. of water  $= 7$  atoms, and at about  $380^\circ$  the 4 remaining atoms of water are expelled. This salt is insoluble in alcohol. When a solution of the preceding salt with the addition of half as much acid as it already contains is evaporated, it forms a mass of acicular prisms  $= 2\text{NaO}, \text{HO}, \overline{\text{Ci}}$ . It has a pleasant subacid taste. When as much citric acid as it already contains, is added to a solution of the first salt, a gummy or very



difficultly crystallizable mass is obtained on evaporation  $= \text{NaO}, 2\text{HO}, \overline{\text{Ci}}$ . It is sparingly soluble in alcohol, from which it is deposited in small crystalline grains.

*Citrate of Lime*,  $3\text{CaO}, \overline{\text{Ci}}, 4\text{HO}$ , is thrown down on mixing solutions of chloride of calcium and citrate of soda; at first the precipitate is redissolved, but afterwards becomes permanent; it is very sparingly soluble in water, but more so in cold than in warm water, so that the cold solution becomes turbid when heated, and again transparent on cooling. This salt is not precipitated from its solution in hydrochloric, nitric, or acetic acid, by excess of ammonia, so that in the analyses of the juices of plants, the citric acid may thus be separated from the other acids, the lime salts of which are so precipitated. When the filtered liquor is afterwards boiled, it deposits the citrate of lime, to separate which it should be filtered whilst boiling hot. At  $212^\circ$  this citrate of lime parts with 3 atoms of water, retaining 1 atom. When citric acid is heated with excess of lime water a *basic* salt falls  $= 3\text{CaO}, \overline{\text{Ci}}, + \text{CaO} + \text{HO}$ ; at  $212^\circ$  it loses its atom of water of crystallization. A hot saturated solution of either of the preceding citrates in citric acid, deposits small crystals, which, however, are decomposed by water, and leave the basic salt.

*Citrate of Baryta*,  $3\text{BaO}, \overline{\text{Ci}} + 7\text{HO}$ , is precipitated in the form of a white powder, on dropping a solution of citrate of soda into chloride of barium. At  $300^\circ$  this salt parts with 6 atoms of water, and at  $374^\circ$  it becomes anhydrous. If a boiling solution of chloride of barium with free citric acid be mixed with a boiling solution of soda, so that the first formed precipitate may be redissolved, a crystalline powder is deposited on cooling, which may be represented by the formula  $2\text{BaO}, \text{HO}, \overline{\text{Ci}} + 3\text{BaO}, \overline{\text{Ci}} + 7\text{HO}$ ; that is, a double salt composed of bibasic and tribasic citrates. On evaporating a boiling solution of acetate of baryta, supersaturated by acetic acid, the same salt is formed.

*Citrate of Magnesia*,  $3\text{MgO}, \overline{\text{Ci}}$ , is a very soluble salt; it does not crystallize with excess of acid, but on evaporation gummy residues are obtained.

*Citrate of Manganese*,  $3\text{MnO}, \overline{\text{Ci}}$ , resembles the magnesian salt. The salt  $= 2\text{MnO}, \text{HO}, \overline{\text{Ci}}$ , is a heavy, tasteless, crystalline powder, formed by digesting carbonate of manganese in a hot solution of citric acid; it is not soluble in water, but very soluble in hydrochloric, and less so in acetic acid.

*Citrate of Protoxide of Iron*,  $3\text{FeO}, \overline{\text{Ci}}$ , forms small prismatic crystals. The mother-liquor is not precipitated by caustic potassa, but alcohol throws down from it a white flocculent precipitate, which speedily oxidizes and becomes brown by exposure to air. *Citrate of peroxide of iron* is formed by saturating citric acid with hydrated peroxide; it is uncrystallizable, and precipitated in brown flocks by alcohol.

*Citrate of Zinc*,  $3\text{ZnO}, \overline{\text{Ci}}$ , is thrown down as a crystalline powder on dissolving carbonate of zinc in a solution of citric acid; when boiling citric acid is saturated with carbonate of zinc, a dense basic salt falls as the liquor cools.

*Citrate of Cobalt*,  $3\text{CoO}, \overline{\text{Ci}}$ , is formed by saturating the acid with

carbonate of cobalt; the solution, left to spontaneous evaporation, concretes into a red paste, which dries into a bulky rose-colored powder. If it be evaporated by heat it leaves a violet-colored mass, soluble in water, and precipitated from its aqueous solution by alcohol.

*Citrate of Nickel*,  $3\text{NiO}, \overline{\text{Ci}}$ , resembles the preceding, but is green.

*Citrate of Copper*. Citrate of soda produces no precipitate with acetate of copper, even when boiled; but when a mixed solution of acetate of copper and citric acid is boiled, a green crystalline powder falls. This salt is also formed by boiling carbonate of copper in a saturated solution of citric acid. The formula of this compound, according to Liebig, is  $3\text{CuO}, \overline{\text{Ci}} + \text{CuO}$ . When a solution of this salt in caustic ammonia is mixed with alcohol, a dark blue oil-like liquid separates, which has no tendency to crystallize.

*Citrate of Lead*,  $3\text{PbO}, \overline{\text{Ci}} + \text{HO}$ , falls on mixing a solution of citrate of soda with excess of acetate of lead; the precipitate should be washed with alcohol, for water resolves it into a soluble bibasic salt  $= 2\text{PbO}, \text{HO}, \overline{\text{Ci}} + 2\text{HO}$ , and a surbasic salt  $= 3\text{PbO}, \overline{\text{Ci}} + 3\text{PbO}$ . (LIEBIG.)

*Citrate of Antimony* has not been examined, but Thaulow obtained a *citrate of potassa and antimony*,  $= 3\text{KO}, \overline{\text{Ci}}, + \text{Sb O}_3, \overline{\text{Ci}} + 5\text{HO}$ , by digesting oxide of antimony in acid citrate of potassa; it forms hard brilliant white prisms which lose their water at  $212^\circ$ .

*Citrate of Black Oxide of Mercury*,  $3\text{Hg}_2\text{O}, \overline{\text{Ci}}$ , is a white crystalline powder formed by double decomposition, or by digesting the oxide in the acid: it is decomposed by boiling water into a soluble and insoluble citrate.

*Citrate of Red Oxide of Mercury*,  $3\text{HgO}, \overline{\text{Ci}}$ , is obtained by dissolving the freshly-precipitated and moist oxide in a warm solution of citric acid; on cooling, the salt falls in the form of a white powder. It may also be formed by double decomposition.

*Citrate of Silver*,  $3\text{Ag O}, \overline{\text{Ci}} + \text{HO}$ , falls in the form of a brilliant white precipitate, on adding a solution of a citrate to a soluble salt of silver. When washed, and dried below  $60^\circ$ , it retains its atom of water, but loses it at about  $80^\circ$ . On contact of an incandescent body it burns with a slight explosion, leaving metallic silver mixed with charcoal.

**ACTION OF HEAT ON CITRIC ACID.** When crystallized citric acid is heated above its point of fusion, it enters into ebullition, and loses water without evolving empyreumatic products; and if the heat be withdrawn as soon as white fumes and inflammable gases are evolved, and the residue dissolved in water and crystallized, the *ordinary acid*, namely,  $\overline{\text{Ci}}, 4\text{HO}$ , is again obtained.

If the distillation be continued as long as inflammable gas and vapor is disengaged, the residue is then no longer citric acid; it is yellow, soluble in ether, and possesses all the properties of *hydrated aconitic acid*. In this case, 1 atom of the crystallized citric acid, losing 4 atoms of water, becomes *anhydrous*, and consequently  $= \text{C}_{12} \text{H}_5 \text{O}_{11}$ ; this anhydrous citric acid is then resolved by the further action of heat, into the following products, namely,



|  |             |
|--|-------------|
| 1 atom of hydrated aconitic acid ..... | C 4 H2 O 4  |
| 1     "     acetone .....              | C 3 H3 O    |
| 4     "     carbonic oxide .....       | C 4     O 4 |
| 1     "     carbonic acid   .....      | C       O 2 |
|  | <hr/>       |
|  | C12 H5 O11  |

XVII. ACONITIC ACID.  $C_4 H O_3$ ,  $HO = \overline{Aco}$ ,  $HO$ . *Equisetic Acid. Citridic Acid* (of Baup). This acid was discovered in 1820, by Peschier; it was soon afterwards examined by Bennerscheidt. In 1828 Braconnot obtained a peculiar acid from several species of *equisetum* (*Ann. Ch. et Ph.*, xxxix. 1), which Regnault recognized as aconitic acid. Dahlström and Berzelius, in 1834, showed the conversion of citric into aconitic acid, and L. A. Büchner examined its salts. In aconite and in the *equisetums* this acid chiefly occurs combined with lime, forming a salt which is held in solution in the sap of those plants. Büchner precipitates it in the form of *aconitate of lead*, which he decomposes by sulphuretted hydrogen.

The preparation of aconitic acid from citric acid consists in heating the latter in a capsule on a sand heat, and stirring it till the residue has a bitter as well as a sour taste ; the mass is then pulverised, and digested in ether, which dissolves the aconitic acid, leaving the bitter product and the undecomposed citric acid. The properties, however, of this acid as obtained from the three above-mentioned sources, are not absolutely identical, though it gives the same results on analysis.

The ethereal solution of the aconitic acid deposits it on evaporation in confused crystalline crusts, colorless, sour, inodorous, and not volatile. It is very soluble in water, and in alcohol, and cannot be isolated in an anhydrous state. Heated up to 265° it becomes colored, fuses at 285°, and is decomposed at 320°. This acid appears to be *monobasic*, and consists, as it exists in combination with bases, of

|                               |   |     |    |     |        |
|-------------------------------|---|-----|----|-----|--------|
| Carbon .....                  | 4 | ... | 24 | ... | 48·98  |
| Hydrogen .....                | 1 | ... | 1  | ... | 2·04   |
| Oxygen .....                  | 3 | ... | 24 | ... | 48·98  |
| <hr/>                         |   |     |    |     |        |
| Anhydrous aconitic acid ..... | 1 |     | 49 |     | 100·00 |

The *hydrated acid* contains

|                               |   |     |    |     |        |
|-------------------------------|---|-----|----|-----|--------|
| Anhydrous aconitic acid ..... | 1 | ... | 49 | ... | 84·48  |
| Water .....                   | 1 | ... | 9  | ... | 15·52  |
| <hr/>                         |   |     |    |     |        |
| Hydrated aconitic acid .....  | 1 |     | 58 |     | 100·00 |

*Aconitates.* The soluble aconitates occasion white precipitates in solutions of acetate of lead and of nitrate of silver, and these precipitates never acquire a crystalline character, even when boiled, or long left in the liquid ; but there is no specific test by which the aconitic acid can be recognised in its salts.

*Aconitate of Ammonia*, evaporated in vacuo over chloride of calcium, yields an uncrystallizable gummy salt. The *binaconitate* forms small groups of acicular crystals. *Aconitate of potassa* is not crystallizable. *Aconitate of soda* is very soluble, and obtained with difficulty in the form

of a crystalline crust. It is soluble in alcohol. *Aconitate of lime* is deposited in the form of difficultly soluble prismatic crystals, when a mixture of the solutions of aconitate of soda and chloride of calcium is slowly evaporated. When a somewhat dilute solution of aconitic acid is saturated by carbonate of lime, the salt assumes a much more soluble condition, though on evaporating this solution it reverts to the difficultly-soluble state. This change belongs to many other salts, and explains how it is that such difficultly-soluble salts may be contained in the sap of plants, which become insoluble in the same sap after they have been separated by evaporation. *Aconitate of baryta*, when formed by double decomposition, falls in a semi-gelatinous state, and does not become granular, either by remaining in the liquor or by boiling, so that it is very difficult of edulcoration. It dries into a shrunk mass resembling hydrated alumina. It retains 2 atoms of water = 12.5 per cent. till heated to  $230^{\circ}$ , when it becomes anhydrous; it may then be heated to  $390^{\circ}$  without further change. It is very sparingly soluble in water, but dissolves in excess of aconitic acid. *Aconitate of magnesia* is very soluble; it abounds in the sap of the *Equisetum hyemale*. *Aconitate of zinc* is very soluble. *Aconitate of peroxide of iron* is thrown down by double decomposition in the form of a brown precipitate. *Aconitate of copper*, formed by saturating a warm solution of the acid by carbonate of copper, yields a blue solution, from which the salt separates on evaporation, in crystalline crusts. *Aconitate of mercury* forms a white powder with both oxides; the salt of the black oxide is immediately precipitated; that of the red oxide is best obtained by digesting the freshly precipitated oxide in a hot solution of aconitic acid. *Aconitate of silver* is formed by double decomposition, but a solution of aconitic acid occasions no precipitate in nitrate of silver. It is white and pulverulent, but not crystalline. It may be heated to  $300^{\circ}$  without change; at a higher temperature it explodes. It is insoluble in water, and blackens by exposure to light. When boiled in water, silver is deposited, no gas is evolved, and another difficultly-soluble silver-salt is formed, which appears to contain a new acid. (BÜCHNER. BERZELIUS.)

XVIII. ITACONIC ACID.  $C_5H_2O_3.HO, = \overline{It},HO$ . *Pyrocitric Acid*. (LASSAIGNE, *Ann. der Pharm.*, viii.) *Citricic Acid*. (BAUP, *Ann. Ch. et Ph.*, xxi., 100.) When either citric or aconitic acid is rapidly heated in a retort up to about  $360^{\circ}$ , two liquids pass into the receiver, the uppermost of which readily dissolves in water, whilst the lowermost, which has an oleaginous appearance, and which is principally *anhydrous itaconic acid*, forms with water a crystalline compound, which, when dissolved in water and evaporated spontaneously, deposits rhombic octohedral crystals of *hydrated itaconic acid*. This acid is intensely sour; it is soluble in 17 parts of water at  $50^{\circ}$ , and in 10 parts at  $70^{\circ}$ , the solubility rapidly increasing with the temperature; it is also soluble in alcohol and in ether. The crystals may be heated to  $250^{\circ}$  without loss of weight; at  $320^{\circ}$  they fuse, exhale an acrid vapor, and sublime without residue. At a higher temperature the acid loses water, and is resolved into anhydrous *citraconic acid*, which distils over. The components of the *anhydrous itaconic acid*, according to Baup (*Berzelius' Lehrbuch*,) and Crasso, (*Ann. Ch. et Ph.*, 3 Ser. I. 316,) appear to be



|                               |   |     |    |     |        |
|-------------------------------|---|-----|----|-----|--------|
| Carbon .....                  | 5 | ... | 30 | ... | 53·57  |
| Hydrogen .....                | 2 | ... | 2  | ... | 3·57   |
| Oxygen .....                  | 3 | ... | 24 | ... | 42·86  |
| <hr/>                         |   |     |    |     |        |
| Anhydrous itaconic acid ..... | 1 |     | 56 |     | 100·00 |

And the crystals of the *hydrated acid* are constituted of

|                                  |   |     |    |     |        |
|----------------------------------|---|-----|----|-----|--------|
| Anhydrous itaconic acid .....    | 1 | ... | 56 | ... | 86·16  |
| Water .....                      | 1 | ... | 9  | ... | 13·84  |
| <hr/>                            |   |     |    |     |        |
| Crystallized itaconic acid ..... | 1 |     | 65 |     | 100·00 |

*Itaconates.* These salts have been principally studied by Baup, under the name of *citracates*, and by Crasso (*Ann. Ch. et Ph.*, 3ème Ser. I. 323.) The itaconic acid produces a white precipitate in the acid and in the basic salts of lead, and in common with certain other organic acids and salts, gives a red tint to solutions of the persalts of iron. It forms neutral and acid salts. The *itaconates of ammonia*, *potassa* and *soda*, are very soluble and deliquescent, and not crystallizable. The *binitaconates* of the same bases, are crystallizable and less soluble. The *itaconates of lime* and *baryta* and *strontia* are all crystallizable. *Itaconate of magnesia* is a gum-like salt, but the *binitaconate* forms lamellar crystals. *Itaconate of lead* is a white powder not perfectly insoluble in water. *Itaconate of copper* forms small difficultly soluble, blue crystals. *Itaconate of silver* is precipitated both by the free acid and its salts, in the form of a white, anhydrous, and almost insoluble powder. It deflagrates when heated.

XIX. CITRACONIC ACID.  $C_5H_2O_3 + HO$ . (ROBIQUET. BAUP. *Ann. Ch. et Ph.*, LXV. 68, and LXI. 182.) *Citribic acid* (of Baup). When itaconic acid is distilled, it yields a limpid oily liquid, which is *anhydrous citraconic acid*. Exposed to the air it absorbs moisture and forms a *crystalline hydrate*, which, when heated is again resolved into water and anhydrous acid. It will be observed that the elements of this acid are the same as those of the preceding, with which it is represented as isomeric.

The *citraconates* in many respects closely resemble the salts of the itaconic acid; there is also the same tendency to the formation of neutral and of acid salts, in respect to both acids. There is a peculiarity belonging to the citraconates of lead and of silver, which is, that those salts, when boiled in a moderately strong solution of citraconic acid, dissolve, and are deposited in a crystalline form as the liquor cools, which is not the case when the corresponding itaconates are similarly dissolved in a solution of itaconic acid. These citraconates also include an atom of water, which however is expelled at  $212^\circ$ , when the crystals become opaque and crumble. The superior solubility of the citraconic acid is perhaps its leading distinctive character, but, as Liebig remarks, although the ultimate composition of the aconitic, itaconic, and citraconic acids is apparently accurately determined, they require re-examination, especially in reference to their combining equivalents. The aconitic acid will probably be found to be tribasic, and one of the others bibasic: at all events the existence of a neutral salt of silver containing water of crystallisation, is at present an anomaly. The principal *citraconates* have been described by Crasso.

XX. MALIC ACID.  $C_8 H_4 O_8, 2HO = \overline{Ma}, 2HO$ . *Sorbic Acid*. (DONOVAN.) The existence of a peculiar acid in the juice of apples was first shown by Scheele in 1784; he obtained it by adding solution of acetate of lead to the expressed juice of unripe apples, by which a *malate of lead* was formed, and afterwards decomposed by sulphuric acid. Vauquelin obtained it by a similar process, from the juice of the *house-leek*. The same acid exists, according to Braconnot and Houton-Labillardière, in the berries of the *Sorbus aucuparia*, or *mountain-ash* (*Ann. Ch. et Ph.*, viii. 214), from which it was first obtained by Donovan in 1815, who has given the following process for its preparation. (*Phil. Trans.*, 1815.) Express the juice of the ripe berries, clarify it by boiling and adding white of egg, and filter; then add solution of acetate of lead, and wash the resulting precipitate with cold water; then pour boiling water upon the filter, and allow it to pass through the precipitate into glass jars: after some hours crystals are deposited, which are to be boiled with 2·3 times their weight of diluted sulphuric acid of specific gravity 1·090. The clear liquor is to be poured off, and, while still hot, a stream of sulphuretted hydrogen is to be passed through it, to precipitate the remaining lead; the liquid is then filtered, and when boiled so as to expel the excess of sulphuretted hydrogen, is a solution of the pure vegetable acid.

Braconnot procures this acid by saturating the juice of the scarcely-ripe berries with chalk; during evaporation, *malate of lime* falls, which he decomposes by carbonate of soda; the *malate of soda* is decomposed by acetate of lead, and treated by sulphuretted hydrogen. (*Ann. Ch. et Ph.*, vi.)

According to Liebig (*Ann. Ch. et Ph.*, xliii. 259, and lii. 434), pure malic acid is obtained by boiling the juice with animal charcoal, filtering, adding a little potassa, evaporating, and adding alcohol to precipitate bitartrate of potassa: then distil off the alcohol, and reduce the residue to the consistency of syrup, and again add alcohol, which throws down mucilage. The residue of the second distillation, diluted and mixed with acetate of lead, yields *malate of lead*, which is washed, and decomposed by sulphuretted hydrogen: to complete the purification of the acid, its solution is concentrated, diluted by alcohol, and half saturated by ammonia: the *bimalate of ammonia* is crystallized, and used as a source of *malate of lead*, to be decomposed as before.

Hagen obtained malic acid as follows: the expressed juice of the mountain-ash berries was mixed in a copper pan with levigated hydrate of lime, care being taken to leave the fluid sensibly sour. It was boiled for some hours, during which a pungent vapor escaped, and neutral malate of lime fell, which was removed by a ladle: when this ceased, the vessel was allowed to cool, and a little more of the malate fell: if the original juice is at first saturated with lime (instead of being left acid) the precipitated malate is mixed with much coloring matter. The neutral malate of lime is dissolved in dilute nitric acid (1 acid + 10 water), filtered, and evaporated; on cooling, colorless crystals of malate of lime form, which must be washed with cold water, dissolved in boiling water, and precipitated by acetate of lead: the lead salt is then decomposed by sulphuretted hydrogen, and the malic acid obtained pure by evaporation. (*Mem. Chem. Soc.*, I. 28.) Everett has recommended



the expressed juice of the culinary rhubarb (*Rheum rhaponticum*), as a source of malic acid. It contains, in the imperial gallon, about 2·3 ounces of malic acid and 6 drachms of oxalic acid. (*Mem. Chem. Soc.*, Jan., 1843.)

Malic acid is usually obtained in the state of a colorless liquid, very sour, and scarcely susceptible of regular crystallization, though when carefully evaporated it concretes into mamillary masses of imperfect acicular crystals. It is deliquescent, and very soluble in alcohol and water. Nitric acid converts it into oxalic acid. The changes which this acid suffers by heat will be afterwards noticed.

Malic acid is *bibasic*; the *anhydrous acid* is composed, according to Liebig, (*Ann. Ch. et Ph.*, xliii. 266, and lxviii. 66) of

|                            |   |      |     |      | Liebig. |
|----------------------------|---|------|-----|------|---------|
| Carbon .....               | 8 | .... | 48  | .... | 41·35   |
| Hydrogen .....             | 4 | .... | 4   | .... | 3·45    |
| Oxygen .....               | 8 | .... | 64  | .... | 55·20   |
| <hr/>                      |   |      |     |      |         |
| Anhydrous malic acid ..... | 1 |      | 116 |      | 100·00  |
|                            |   |      |     |      | 100·000 |

And the *hydrated crystalline acid* contains

|                           |   |      |     |      |        |
|---------------------------|---|------|-----|------|--------|
| Anhydrous malic acid..... | 1 | .... | 116 | .... | 86·57  |
| Water .....               | 2 | .... | 18  | .... | 13·43  |
| <hr/>                     |   |      |     |      |        |
| Hydrated malic acid ..... | 1 |      | 134 |      | 100·00 |

*Malates.* Braconnot, Liebig, and more especially Hagen, have examined these salts. They are mostly soluble in water, and those which are not so are soluble in dilute nitric acid. They are insoluble in alcohol, with the exception of the malate of peroxide of iron. Lime water is not rendered turbid by malic acid, but on evaporating the solution, crystalline malate of lime separates, which is redissolved by boiling. These characters are useful in distinguishing malic acid from oxalic, tartaric, racemic, and citric acid. The peculiar and brilliant crystalline appearance which recently precipitated malate of lead gradually assumes when left in the liquor, is very characteristic of that salt. There are two series of malates, namely, *neutral* =  $2\text{MO}, \overline{\text{Ma}}$ , and *acid* =  $\text{MO}, \text{HO}, \overline{\text{Ma}}$ .

*Malate of Ammonia.*  $2\text{NH}_4\text{O}, \overline{\text{Ma}}$ . This salt, when neutral, is not crystallisable, and very deliquescent. *Acid malate of ammonia*,  $\text{NH}_4\text{O}, \text{HO}, \overline{\text{Ma}}$ , forms limpid crystals resembling those of rock crystal, soluble in 8 parts of cold water, but more soluble at  $212^\circ$ . This salt is most economically prepared from the crude malate of lead obtained by adding acetate of lead to the expressed juice of apples, or of mountain-ash berries gathered when they are just beginning to redden. The precipitated malate of lead is then diffused in water heated to about  $150^\circ$ , and decomposed by dilute sulphuric acid, leaving the latter a little in excess, so that a drop of the liquor tested by chloride of barium gives a slight cloud; the whole is then boiled and filtered, and the red liquor which is obtained, evaporated to one-half; this is then divided into two equal portions, one of which is saturated by carbonate of ammonia; the other portion is then added, and the whole evaporated to a syrupy consistence; after about 24 hours, a crop of colored crystals is obtained; these must

be redissolved in boiling water, decolorized by purified animal charcoal, and on evaporating the filtered liquor, pure acid malate of ammonia is obtained. The presence of iron must be carefully avoided in these operations, as it renders the crystals permanently colored; and if sulphate of ammonia be present it prevents the crystallisation of the whole of the malate. (LIEBIG.)

The *neutral malates of potassa and of soda* are uncrystallisable; their *acid malates* are crystallisable, but very soluble.

*Malate of Lime*,  $2\text{CaO}, \overline{\text{Ma}}$ . When a cold solution of malic acid is saturated with hydrate of lime, filtered, and evaporated *in vacuo*, small brilliant crystals are deposited, which are very soluble, and contain 2 atoms of water, one of which is disengaged at  $300^\circ$ ; at  $390^\circ$  the salt becomes anhydrous. If, instead of evaporating at a low temperature, the solution be boiled, a granular precipitate of the anhydrous malate falls. When a solution of acid malate of lime is neutralised by an alkali, and evaporated, a crystallised salt is obtained, which contains none of the alkali, but which is a neutral malate of lime with 5 atoms of water = 20·3 per cent. These crystals lose 1 atom of their water at  $212^\circ$ , and at  $300^\circ$  they become anhydrous.

*Acid Malate of Lime*,  $\text{CaO}, \text{HO}, \overline{\text{Ma}} + 6\text{HO}$ . This salt, frequently called *bimalate of lime*, may be formed by dissolving the neutral malate in hot malic acid, or in a boiling mixture of 1 part of nitric acid and 10 of water. On evaporation, rhombic octohedrons are obtained, containing 24·8 per cent. of water, = 6 atoms, 2 atoms of which go off at  $212^\circ$ , and the remaining 4 atoms at  $365^\circ$ , leaving  $\text{CaO}, \text{HO}, \overline{\text{Ma}}$ . The crystals are soluble in 20 parts of cold, and in their own weight of boiling water. (HAGEN.)

*Malate of Baryta*,  $2\text{BaO}, \overline{\text{Ma}}, 4\text{HO}$ . When carbonate of baryta is added to a solution of malic acid, a neutral malate is not obtained, so that to saturate the acid, it is necessary afterwards to add an adequate quantity of baryta water; on careful evaporation, a crystalline deposit of the salt having the above formula, is obtained. If the solution be rapidly evaporated, even when it contains excess of acid, the neutral salt, in its anhydrous state, is deposited in the form of a granular crust, insoluble in water. The crystallised hydrated salt, on the contrary, is soluble in cold water. No *acid malate of baryta* has been obtained.

*Malate of Magnesia*. The neutral salt is obtained by saturating a solution of malic acid with *magnesia alba*. The filtered liquor forms, on careful evaporation, small cubical crystals, containing about 36 per cent. of water, and therefore =  $2\text{MgO}, \overline{\text{Ma}}, + 10\text{HO}$ . They effloresce in the air, and when dried at  $212^\circ$ , retain 1 atom of water only. The crystals dissolve in about 28 parts of cold water, but are much more soluble at  $212^\circ$ . Alcohol, added to their aqueous solution, throws down a bulky white precipitate, which if the liquor be boiled, acquires a viscid consistence. The *acid malate*, =  $\text{MgO}, \text{HO}, \overline{\text{Ma}}, + 3\text{HO}$ , crystallises in flattened 6-sided prisms: at  $212^\circ$  they lose 2 atoms of their water of crystallisation.

*Malate of Manganese*,  $2\text{MnO}, \overline{\text{Ma}}$ , forms a deliquescent gumlike saline mass. When malic acid is added to its concentrated solution, a granular precipitate of the *acid malate* ensues, which, dissolved in boiling water, yields red crystals on cooling, soluble in about 40 parts of cold water. (BRACONNOT.)

*Malate of Protoxide of Iron* has not been examined.



*Malate of Peroxide of Iron* is an uncrystallisable salt, very soluble in water and in alcohol; its aqueous solution is not precipitated by caustic alkali, and when digested with hydrated peroxide of iron, deposits a basic malate.

*Malate of Zinc*,  $2\text{ZnO}, \overline{\text{Ma}}, 6\text{HO}$ . When a solution of malic acid is saturated at the temperature of  $90^\circ$ , with oxide of zinc, small hard brilliant crystals of the above salt are obtained, very difficultly soluble in cold water, and depositing a basic salt in boiling water. A concentrated solution of hydrated oxide of zinc in boiling malic acid forms a transparent jelly on cooling, which gradually changes into a crystalline basic precipitate, containing between 44 and 48 *per cent.* of oxide; or, 8 atoms of oxide of zinc, 3 atoms of malic acid, and 6 of water. The *acid malate of zinc*, formed by dissolving the neutral salt in excess of acid, yields octohedral crystals on evaporation, which require 23 parts of cold water for solution, and are insoluble in alcohol. Their formula is  $\text{ZnO}, \text{HO}, \overline{\text{Ma}}, + 3\text{HO}$ . (BRACONNOT. HAGEN.)

*Malate of Copper*. Carbonate of copper is abundantly soluble in an aqueous solution of malic acid, forming a green solution, which evaporated in *vacuo* at  $110^\circ$ , or  $120^\circ$ , yields regular green crystals, leaving a very acid, and nearly colorless mother-liquor. The crystals are very soluble in cold water, and when dried in *vacuo* over sulphuric acid, lose water and become blue. When their concentrated aqueous solution is boiled, it deposits a green powder insoluble in water and acids; if mixed with alcohol, a bluish-green salt separates, which is soluble in water, but it is transformed by boiling into the green insoluble salt. The following are the formulæ of these compounds:

|                                   |  |
|-----------------------------------|--|
| Crystallizable salt .....         | $3\text{CuO}, \overline{\text{Ma}} + 6\text{HO}$ |
| Insoluble salt .....              | $3\text{CuO}, \overline{\text{Ma}} + 4\text{HO}$ |
| Salt precipitated by alcohol..... | $3\text{CuO}, \overline{\text{Ma}} + 5\text{HO}$ |

By saturating a cold solution of malic acid with hydrated oxide of copper, and evaporating the solution at about  $100^\circ$ , large blue crystals of an *acid malate of copper* are obtained  $= \text{CuO}, \text{HO}, \overline{\text{Ma}} + 2\text{HO}$ . It loses its 2 atoms of water of crystallisation at  $212^\circ$ . (HAGEN.)

*Malate of Lead*,  $2\text{PbO}, \overline{\text{Ma}} + 6\text{HO}$ , was obtained by Pelouze by mixing a solution of acid malate of ammonia, or of lime, with acetate of lead, and leaving the resulting precipitate, which contains ammonia or lime, for some time in contact with excess of the acetate of lead, when it gradually forms quadrilateral acicular crystals of a silky lustre: the 6 atoms of water may be expelled by heat. No *acid malate of lead* has been formed. Malate of lead forms double salts with malate of ammonia and of zinc.

*Malate of black oxide of Mercury*,  $2\text{Hg}_2\text{O}, \overline{\text{Ma}}$ , is obtained by double decomposition, as a white insoluble powder. It is blackened by caustic ammonia. *Malate of red oxide of mercury* is obtained as a yellow *basic* salt, by digesting the oxide in malic acid. When this basic salt is dissolved in excess of warm malic acid, it crystallises as the liquor cools.

*Malate of Silver*,  $2\text{AgO}, \overline{\text{Ma}}$ , is an anhydrous white precipitate, sparingly soluble in boiling water, and not much more soluble in malic acid. It dissolves in nitric acid.

XXI. FUMARIC ACID.  $C_4H_2O_4$ ,  $HO = \overline{Fu}$ ,  $HO$ . *Pyromalic Acid. Paramalæic Acid. Lichenic Acid.* The action of heat upon malic acid was first inquired into by Braconnot, in 1818. (*Ann. Ch. et Ph.*, viii. 149.) Lassaigne afterwards examined the products, (*ibid.* xi. 93,) and in 1834, Pelouze discovered that two distinct acids were thus formed, which he termed *malæic* and *paramalæic acid*. (*Ibid.*, lvi. 72.) In 1826, Pfaff discovered a peculiar acid in Iceland moss, to which the name of *Lichenic acid* was given, (*Ann. de Pharm.*, xvii. 148,) and, in 1831, Winkler detected a distinct acid in the *Fumaria officinalis*, which was therefore called *Fumaric acid*, and which, in 1834, was shown by Demarçay to be identical with the paramalæic acid of Pelouze, (*Ann. Ch. et Ph.*, lvi. 429,) while the identity of the lichenic and paramalæic acid was afterwards demonstrated by Schödler. (*Ann. der Pharm.*, xvii. 148.)

To obtain fumaric acid from the *Fumaria officinalis*, the juice of the plant is pressed out and heated up to its boiling-point, to coagulate albumen; it is then filtered, and a solution of acetate of lead is added; the resulting precipitate is then washed, diffused in water, and decomposed by sulphuretted hydrogen; the resulting acid liquor is then boiled, and filtered while hot, and it deposits, on cooling, crystals of fumaric acid, of which more may be obtained by the evaporation of the mother-liquor. To render the crystals perfectly white they must be redissolved in boiling water, and the solution treated with animal charcoal in the usual way. Or the crystallised acid may be dissolved to saturation in hot nitric acid, of the sp. gr. 1.4, by which the coloring matter is destroyed, and colorless crystals deposited on cooling, from which the adhering nitric acid may be separated by redissolving them in boiling water, and recrystallising.

Pelouze converted malic acid into fumaric acid, by heating it in a retort placed in an oil-bath at a temperature of  $300^\circ$ , as long as water distilled over; the residue was a crystalline mass of fumaric acid. If the heat in this case be raised to  $350^\circ$ , the fumaric acid is then converted into malæic acid and water.

Fumaric acid may be obtained from *Iceland moss*, by cutting it up into small pieces, and digesting it for 5 or 6 days in a diluted milk of lime, which abstracts the acid, and leaves the starch and fibre; the whole is then pressed out: the clear liquor is evaporated to half its bulk, acidulated by acetic acid, and heated to its boiling-point, when subacetate of lead is gradually dropped into it as long as a colored precipitate ensues, which contains coloring matter and other substances, and is to be separated by filtering the boiling hot liquor, in which the fumarate of lead is retained in solution, and deposited in acicular crystals as it cools; the lead salt is then to be decomposed by sulphuretted hydrogen, and the resulting fumaric acid purified by the agency of nitric acid as above directed.

The fumaric acid thus obtained is deposited from its hot saturated aqueous solution, in small micaceous crystals or tufts; and from its hot nitric solution, in acicular crystals; it has a slightly sour taste; it requires for solution about 200 parts of cold water, but it is much more soluble in boiling water; it is also soluble in alcohol, and readily soluble in ether. When heated upon a slip of platinum, it volatilises without residue. Fumaric acid is not decomposed by cold sulphuric acid, nor by hot nitric acid, nor when boiled with chloride of gold or platinum, or bichromate



of potassa, or peroxide of lead. Anhydrous fumaric acid has precisely the same equivalent and atomic constitution as the aconitic acid. (p. 1344.)

*Fumarates.* Fumaric acid is regarded as *monobasic*, but it forms basic, neutral, and acid salts. In consequence of the difficult solubility of fumaric acid in water, its salts are best obtained by adding it to an acetic solution of the base, and boiling, when the weaker and volatile acetic acid is expelled. When the salts of the two acids are equally soluble in water, the crystallisation of the fumarate may be accelerated by the addition of alcohol. The fumarates are recognised by the precipitation from them of fumaric acid by the stronger acids, and by the solubility of the lead precipitate in boiling water; in this respect it resembles the malic acid; but malate of lead enters into fusion in boiling water, which is not the case with the fumarate of lead. The fumarates have been especially examined by Rieckher. (BERZELIUS, *Lehrbuch*.)

*Fumarate of Ammonia*,  $\text{NH}_4\text{O}, \overline{\text{Fu}}$ , is formed by saturating the dry crystallised acid with gaseous ammonia; it is very soluble, and, when exposed to air loses ammonia and passes into *bifumarate*, which forms 6-sided prisms, soluble in water, but insoluble in absolute alcohol. They contain no water of crystallisation. When *fumarate of oxide of ethyle* (see *Ethers*) is acted on by ammonia, a white insoluble substance is formed, which has been termed *fumaramide*  $= \text{C}_4 \text{H O}_2 + \text{NH}_2$ .

*Fumarate of Potassa*,  $\text{KO}, \overline{\text{Fu}}$ , crystallises in 4-sided tables, which hold 15 to 16 *per cent.* of water,  $= 2$  atoms. This salt is insoluble in alcohol. At  $212^\circ$  it becomes opaque and anhydrous. It is precipitated by alcohol from its concentrated aqueous solution, in the form of thick drops, which change in 24 hours into a crystalline powder. *Bifumarate of potassa*,  $\text{KO}, \overline{\text{Fu}}, \text{HO}, \overline{\text{Fu}}$ , formed by dissolving an additional atom of fumaric acid in a hot solution of the neutral salt, crystallizes in prisms, which are difficultly soluble in cold water: they lose no water when heated.

*Fumarate of Soda*,  $\text{NaO}, \overline{\text{Fu}}$ , forms silky acicular crystals, containing 3 atoms ( $= 25.12$  *per cent.*) of water of crystallisation; they are very soluble, and, when alcohol is added to their aqueous solution, a crystalline powder is precipitated, which contains only 1 atom of water. At  $212^\circ$  it becomes anhydrous. The *bifumarate* forms crystalline tufts.

*Fumarate of Lime*,  $\text{CaO}, \overline{\text{Fu}}$ , is contained in the *Fumaria officinalis*; it is best formed artificially, by adding fumaric acid to a solution of acetate of lime, boiling, and evaporating: it is deposited in small hard shining crystals, containing 3 atoms ( $25.8$  *per cent.*) of water. It is very difficultly soluble in water, and insoluble in alcohol.

*Fumarate of Baryta*,  $\text{BaO}, \overline{\text{Fu}}$ , is formed by mixing strong hot solutions of fumaric acid and acetate of baryta; small granular crystals are formed, and are immediately deposited on scratching the sides of the glass with a hard substance. This salt is sparingly soluble in water. At  $212^\circ$  it loses about 15 *per cent.* of water.

*Fumarate of Strontia*,  $\text{SrO}, \overline{\text{Fu}}$ , crystallises with 3 atoms of water, (21 *per cent.*,) which is slowly expelled at  $212^\circ$ .

*Fumarate of Magnesia*,  $\text{MgO}, \overline{\text{Fu}}$ , is very soluble, and forms, on evaporation, a gummy mass.

*Fumarate of Peroxide of Iron* falls in the state of a basic salt, on

adding fumarate of potassa to neutral chloride of iron; it is  $\text{Fe}_2 \text{O}_3, 2\overline{\text{Fu}}$ . A *protofumarate of iron* has not been obtained.

*Fumarate of Zinc*,  $\text{ZnO}, \overline{\text{Fu}}$ , forms soluble prismatic crystals, containing 13.1 per cent. of water of crystallisation.

*Fumarate of Copper*,  $\text{Cu O}, \overline{\text{Fu}}$ , is formed by dissolving fumaric acid in a warm solution of acetate of copper; if they are boiled together, no combination ensues. The salt forms a green crystalline powder, containing 3 atoms of water of crystallisation. Its solution in ammonia yields, on spontaneous evaporation, small blue octohedral crystals of a double salt.

*Fumarate of Lead*,  $\text{PbO}, \overline{\text{Fu}}$ , may be formed by double decomposition, or by digesting fumaric acid in a solution of acetate of lead; it is soluble in boiling water, and separates on cooling in micaceous or acicular crystals, containing 2 atoms (10.1 per cent.) of water of crystallisation. When this salt is digested in ammonia, a *basic fumarate* is formed,  $= 2\text{PbO}, \overline{\text{Fu}}$ , which is not rendered anhydrous till dried at  $390^\circ$ .

*Fumarate of Silver*,  $\text{AgO}, \overline{\text{Fu}}$ , is pulverulent, white, and anhydrous. It is soluble in nitric acid. When heated, it explodes like gunpowder.

XXII. MALÆIC ACID. *Malfuric Acid*.  $\text{C}_8 \text{H}_2 \text{O}_6, 2\text{HO} = \overline{\text{Mæl}}, 2\text{HO}$ . When malic acid is subjected to a temperature a little above  $390^\circ$ , Pelouze found it to be almost entirely converted into *malæic acid*. According to Büchner junior, the produce of this acid depends much upon careful manipulation; a capacious retort and receiver should be used, the retort not being more than one-fourth filled with malic acid, and it should be distilled as rapidly as possible. Water first passes over, and then white fumes of malæic acid, which are condensed by the water. As soon as the mass in the retort begins to thicken, the fire should be removed, as the distillation goes on for some time by itself, till congealed fumaric acid remains in the retort. By continuing the distillation, more malæic acid may be procured, but then it is colored, and difficult of purification. The liquor in the receiver is clear, and very sour, and on careful evaporation, leaves *hydrated malæic acid* in transparent rhombic prisms. Its taste is at first sour, and then nauseous, and almost metallic. When it is heated in a retort to  $320^\circ$ , and carefully kept at that temperature as long as it parts with water, the fused *anhydrous malæic acid* remains, and with great care may be distilled over; to effect this, a fresh receiver should be applied, and the neck of the retort greatly inclined; the acid should then be cautiously raised to  $350^\circ$ , when it boils and distils over, a few crystals only of fumaric acid remaining in the retort. If the temperature somewhat exceed  $350^\circ$ , gaseous products are evolved, a part of the acid is decomposed, and that which goes over is much colored. The anhydrous acid has been but little studied; it is solid at common temperatures; it fuses at  $134^\circ$ , and boils at  $350^\circ$ . In the air it gradually attracts moisture, and reverts to the crystalline hydrate; it dissolves pretty rapidly in water, but its relations to alcohol and ether, and to dry ammonia, have not been studied. (BERZELIUS, *Lehrbuch*, iv. 200.) It will be obvious that the aconitic, fumaric, and malæic acids, are isomeric, and that the two former have the same equivalent. Regarding the malæic acid as *bibasic*, its equivalent in the anhydrous state will be 98, and the equivalent of the hydrated acid 116.



*Malæates.* These salts closely resemble the isomeric aconitates and fumarates, but they differ from the aconitates in producing a precipitate in solution of acetate of lead, which though at first pulverulent, soon changes into a crystalline state; whereas the aconitate of lead remains in its original uncrystalline condition, even when heated. The fumarates are distinguished from the malæates, by the precipitate of fumaric acid which they afford with other acids, when in not too dilute solution; or when the decomposed fumarate is insoluble, the fumaric acid remains undissolved.

The malæates of the alkalis are very soluble and difficultly crystallizable. Lime water is not rendered turbid by malæic acid; in baryta water it produces a white precipitate, which gradually changes into a crystalline deposit soluble in pure water. A mixture of malæate of potassa and chloride of barium deposits, after some days, acicular crystals, which are very sparingly soluble in water. The above-mentioned crystalline malæate of lead is, according to Pelouze,  $2\text{PbO}, \overline{\text{Mæl}}, + 3\text{HO}$ . The soluble malæates produce a white precipitate in the soluble salts of silver, which, when dried, deflagrates on being heated. If left in the liquor, it acquires a crystalline appearance, and is an anhydrous malæate,  $= 2\text{AgO}, \overline{\text{Mæl}}$ . When a moderately strong solution of malæic acid is mixed with nitrate of silver, brilliant acicular crystals of an acid salt are gradually deposited,  $= \text{AgO}, \text{HO}, \overline{\text{Mæl}}$ . (LIEBIG.)

XXIII. BENZOIC ACID. The history of benzoic acid has of late years assumed a highly important aspect; it has become the foundation of a series of very interesting experimental researches, and of new theories and generalisations; and embraces some of the most explicit cases of metamorphosis and substitution, which occur in organic chemistry. The extent and complexity of these inquiries, and the number of new compounds which have been discovered in their pursuit, renders the arrangement of the whole a matter of much difficulty, especially where, as in the present case, it becomes necessary to condense and abridge, to the utmost possible extent, and at the same time to maintain what may be termed the integrity of the narrative; this, indeed, I have found almost unattainable as respects the details of description. I therefore subjoin a tabular view of the different compounds which have to be noticed, so arranged as to show their mutual connexion, and relative composition, and to illustrate their theoretical relations, and shall then proceed separately to describe them, but in a different order, having reference rather to the convenience of the student, than to any accordance with theory or hypothesis. In the following table I have assumed the *fundamental hydrocarbon* of the series to be  $\text{C}_{14}\text{H}_5$ , and to this, in common with Löwig, and some other systematic writers, I have applied the term *Benzoyle*; so that the original benzoyle, or benzule of Wöhler and Liebig, which at the period of their researches was a hypothetical body, but which has since been isolated by Ettling, and which is  $\text{C}_{14}\text{H}_5\text{O}_2$ , becomes of course one of the *oxides* of the preceding radical: it may also be necessary to add, that I have described or adverted to several compounds of this benzoyle series which are not included in the following list, and that on the other hand, a few combinations generally considered as belonging to it, have been intentionally omitted.

|   |  |  |
|---|--|--|
| Benzoyle }<br>Benzule }   | C <sub>14</sub> H <sub>5</sub> .....   | Bz   |
| Hydruret of Benzoyle }<br>Picramyle<br>Stilbene }   | C <sub>14</sub> H <sub>6</sub> .....   | Bz H                                       |
| Benzoic oxide }<br>Oxide of Benzoyle<br>Benzoyle (Wöhler and Liebig) }                                      | C <sub>14</sub> H <sub>5</sub> O <sub>2</sub> .....  | Bz O <sub>2</sub>                          |
| Hydruret of Oxide of Benzoyle }<br>Hydruret of Benzule<br>Bitter almond oil<br>Oxide of Picramyle (Löwig) } | { C <sub>14</sub> H <sub>6</sub> O <sub>2</sub><br>C <sub>14</sub> H <sub>5</sub> O <sub>2</sub> + H }   | Bz O <sub>2</sub> , H                      |
| Chloride of Oxide of Benzoyle ....  | C <sub>14</sub> H <sub>5</sub> O <sub>2</sub> + Cl .....   | Bz O <sub>2</sub> , Cl                     |
| Iodide of ditto ....  | C <sub>14</sub> H <sub>5</sub> O <sub>2</sub> + I.....   | Bz O <sub>2</sub> , I                      |
| Bromide of ditto ....   | C <sub>14</sub> H <sub>5</sub> O <sub>2</sub> + Br .....   | Bz O <sub>2</sub> , Br                     |
| Sulphuret of ditto ....   | C <sub>14</sub> H <sub>5</sub> O <sub>2</sub> + S.....   | Bz O <sub>2</sub> , S                      |
| Amide of ditto }<br>Benzamide   | C <sub>14</sub> H <sub>5</sub> O <sub>2</sub> + NH <sub>2</sub> .....  | Bz O <sub>2</sub> , NH <sub>2</sub>        |
| Bromide of Benzamide .....  | C <sub>14</sub> H <sub>5</sub> O <sub>2</sub> + NH <sub>2</sub> + 2Br  |  |
| Hydrobenzamide }<br>Benzhydramide<br>Benzoline<br>Amarine }   | C <sub>14</sub> H <sub>8</sub> N <sub>2</sub>  |  |
| Nitrobenzoyle .....   | C <sub>14</sub> H <sub>5</sub> N .....   | Bz N                                       |
| Azobenzoyle .....   | C <sub>42</sub> H <sub>15</sub> N <sub>2</sub> .....   | Bz <sub>3</sub> N <sub>2</sub>             |
| Benzoic acid (anhydrous) .....  | C <sub>14</sub> H <sub>5</sub> O <sub>3</sub> .....  | Bz O <sub>3</sub> = $\overline{\text{Bz}}$ |
| Ditto (crystallized).....   | C <sub>14</sub> H <sub>6</sub> O <sub>4</sub> .....  | $\overline{\text{Bz}}$ , HO                |
| Chlorobenzoic acids .....   | { C <sub>14</sub> H <sub>4</sub> O <sub>3</sub> + Cl<br>C <sub>14</sub> H <sub>3</sub> O <sub>3</sub> + Cl <sub>2</sub><br>C <sub>14</sub> H <sub>2</sub> O <sub>3</sub> + Cl <sub>3</sub> |  |
| Bromobenzoic acid .....   | C <sub>28</sub> H <sub>9</sub> O <sub>8</sub> + Br + 2HO   |  |
| Hyposulphobenzoic acid }<br>Sulphobenzoic acid }  | { C <sub>14</sub> H <sub>4</sub> O <sub>3</sub> + S <sub>2</sub> O <sub>5</sub><br>C <sub>14</sub> H <sub>4</sub> O <sub>2</sub> + 2SO <sub>3</sub>  |  |
| Nitrobenzoic acid .....   | C <sub>14</sub> H <sub>5</sub> O <sub>3</sub> + NO <sub>5</sub> .....  | $\overline{\text{Bz}}$ , NO <sub>5</sub>   |
| Hydruret of Sulphobenzoyle }<br>Sulphuret of Picramyle }  | C <sub>14</sub> H <sub>6</sub> S <sub>2</sub>  |  |
| Benzamic acid.....  | C <sub>14</sub> H <sub>4</sub> O <sub>3</sub> , NH <sub>2</sub> + HO   |  |
| Benzole }<br>Benzine }  | C <sub>12</sub> H <sub>6</sub> = C <sub>12</sub> H <sub>5</sub> + H  |  |
| Azobenzide .....  | C <sub>12</sub> H <sub>5</sub> N   |  |
| Nitrobenzide .....  | C <sub>12</sub> H <sub>5</sub> NO <sub>4</sub>   |  |
| Sulphobenzide.....  | C <sub>12</sub> H <sub>5</sub> SO <sub>2</sub>   |  |
| Chloride of Benzole .....   | C <sub>12</sub> H <sub>6</sub> Cl <sub>6</sub>   |  |
| Bromide of Benzole .....  | C <sub>12</sub> H <sub>6</sub> Br <sub>6</sub>   |  |
| Chlorobenzoine .....  | C <sub>12</sub> H <sub>3</sub> Cl <sub>3</sub>   |  |
| Benzoine.....   | C <sub>28</sub> H <sub>12</sub> O <sub>4</sub>   |  |
| Benzile .....   | C <sub>28</sub> H <sub>10</sub> O <sub>4</sub>   |  |
| Benzilic acid .....   | C <sub>28</sub> H <sub>11</sub> O <sub>5</sub> + HO  |  |
| Hydrocyanate of Benzile .....   | C <sub>28</sub> H <sub>10</sub> O <sub>4</sub> + 2[C <sub>2</sub> N, H]  |  |
| Benzimide .....   | C <sub>28</sub> H <sub>11</sub> O <sub>4</sub> N   |  |
| Mandelic acid }<br>Formobenzoilic acid }  | C <sub>16</sub> H <sub>7</sub> O <sub>5</sub> + HO   |  |
| Benzoate of hydruret of Benzule   | C <sub>42</sub> H <sub>18</sub> O <sub>8</sub>   |  |



|                                |   |                                     |
|--------------------------------|---|-------------------------------------|
| Benzostilbine .....            | C <sub>31</sub> H <sub>11</sub> O <sub>2</sub>                |                                     |
| Benzolon .....                 | C <sub>11</sub> H <sub>4</sub> O                              |                                     |
| Hydrocyanate of Benzoine.....  | C <sub>46</sub> H <sub>18</sub> O <sub>4</sub> N <sub>2</sub> |                                     |
| Hippuric acid (anhydrous)..... | C <sub>18</sub> H <sub>8</sub> O <sub>5</sub> N               | $\overline{\text{Hip}}$             |
| Ditto (crystallized) .....     | C <sub>18</sub> H <sub>9</sub> O <sub>6</sub> N               | $\overline{\text{Hip}} + \text{HO}$ |
| Amygdaline.....                | C <sub>40</sub> H <sub>27</sub> O <sub>22</sub> N             |                                     |
| Amygdalic acid .....           | C <sub>40</sub> H <sub>26</sub> O <sub>24</sub>               |                                     |

BENZOIC ACID. C<sub>14</sub> H<sub>5</sub> O<sub>3</sub>, HO =  $\overline{\text{Bz}}$ , HO. This substance is described as long ago as 1608, by Blaise de Vigenère, under the name of *flowers of benzoin*. (*Treatise on Fire and Salt*.) It is found ready formed in *benzoin*, the resinous exudation of the *Styrax Benzoin*, a tree growing in Sumatra, Borneo, and Java. (MARSDEN, *Hist. of Sumatra*; CRAWFORD, *Hist. of Ind. Archip.*) *Tolu* and *Peru Balsam* also contain benzoic acid, in common with *Cinnamic acid*; and it is a product of the oxidization of *bitter almond oil*, as will afterwards be shown.

*Benzoic acid* is almost always obtained from benzoin, either by sublimation, or in the humid way, by the action of bases: the amount of the product is extremely various, depending partly upon the quality of the benzoin, and partly upon the process selected, and the care with which it is conducted; it fluctuates from 4 to 10 per cent. The process usually resorted to consists in coarsely pulverising the benzoin, and heating it in a shallow iron, or other vessel, over the top of which a sheet of coarse blotting-paper is stretched, surmounted by a cone of pasteboard or thick paper; or by a wooden vessel or receiver, if the operation is carried on upon the large scale. The layer of benzoin should not be more than 2 or 3 inches in thickness, and the heat gradually and regularly applied, so as slowly to sublime the acid, the vapor of which, passing through the bibulous diaphragm, condenses in a crystalline form in the cone or recipient, whilst the empyreumatic oil at the same time evolved, is retained and absorbed by the paper. (MOHR.) Benzoic acid may also be obtained by triturating pulverized benzoin with a fourth of its weight of dry carbonate of soda, adding water sufficient to form a pasty mixture, and digesting at a temperature of 130° to 140°, for about 36 hours; more water is then added, and the whole boiled together, by which a liquor is obtained holding carbonate and benzoate of soda, and resin, in solution; this liquor is then saturated with sulphuric acid, and filtered whilst boiling hot; on cooling, benzoic acid crystallizes. (BUCHOLZ.) Another process consists in rubbing the benzoin to powder with half its weight of hydrate of lime, and adding 10 parts of water; after the mixture has digested for some hours, it is boiled and filtered; the filtered liquor, and the washings of the residue, are then concentrated by boiling, and saturated, whilst hot, by hydrochloric acid; on cooling, crystallised benzoic acid is deposited, which must be again dissolved and crystallised. (SCHEELE.)

Pure benzoic acid is inodorous; but, as obtained by sublimation, it has a peculiar and agreeable odor, derived from a trace of volatile oil; it generally forms acicular crystals; but, by slow evaporation of its alcoholic solution, or of its solution in neutral carbonate of ammonia, it sometimes forms plates, derived, according to Wackenroder, from a rhombic prism. It has a slightly sour and somewhat acrid taste. It enters into fusion at

about  $250^{\circ}$ , and on cooling, congeals into a white crystalline mass. At about  $295^{\circ}$  it rapidly evaporates and sublimes, its vapor powerfully irritating the throat and eyes. At about  $460^{\circ}$  it boils, and forms a vapor, the specific gravity of which, according to Mitscherlich, (*Poggend.*, xxxi. and xxxv.) is 4.26. This acid requires 200 parts of water at  $60^{\circ}$ , and 30 parts at  $212^{\circ}$ , for its solution; the saturated boiling solution concretes on cooling into a crystalline mass. It dissolves in about twice its weight of alcohol, and this solution is precipitated on dilution with water. It also dissolves in ether, and in fat and volatile oils. In its usual crystalline form it contains an atom of water. The composition of the *anhydrous acid*, as it exists in combination with certain bases, is

|                           |    |     |     |     | Liebig. |     | Berzelius. |     |         |
|---------------------------|----|-----|-----|-----|---------|-----|------------|-----|---------|
| Carbon.....               | 14 | ... | 84  | ... | 74.34   | ... | 74.43      | ... | 74.372  |
| Hydrogen .....            | 5  | ... | 5   | ... | 4.42    | ... | 4.34       | ... | 4.413   |
| Oxygen .....              | 3  | ... | 24  | ... | 21.24   | ... | 21.23      | ... | 21.215  |
| <hr/>                     |    |     |     |     |         |     |            |     |         |
| Anhydrous benzoic acid... | 1  |     | 113 |     | 100.00  |     | 100.00     |     | 100.000 |

The elementary composition of the *crystallized acid* is

|                                  |    |     |     |     | Dumas. |     |        |       |              |       |     |     |     |      |       |
|----------------------------------|----|-----|-----|-----|--------|-----|--------|-------|--------------|-------|-----|-----|-----|------|-------|
| Carbon .....                     | 14 | ... | 84  | ... | 68.85  | ... | 69.25  | } = { | Anhydrous    | }     | 1   | ... | 113 | ...  | 92.62 |
| Hydrogen....                     | 6  | ... | 6   | ... | 4.92   | ... | 4.86   |       | benzoic acid |       |     |     |     |      |       |
| Oxygen.....                      | 4  | ... | 32  | ... | 26.23  | ... | 25.89  |       | Water.....   | 1     | ... | 9   | ... | 7.38 |       |
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| Crystallized }<br>benzoic acid } | 1  |     | 122 |     | 100.00 |     | 100.00 | } = { | <hr/>        |       |     |     |     |      |       |
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afterwards effloresces, and, losing ammonia, passes into an acid salt. This *bibenzoate* is formed in well-defined crystals, when a solution of the neutral salt is left to spontaneous evaporation; when obtained by rapid evaporation, it forms plumose, or granular crystals.

*Benzoate of Potassa*,  $\text{KO}, \overline{\text{Bz}}$ , forms efflorescent plumose crystals, containing 1 atom of water, which is expelled at  $212^\circ$ . When deposited from its alcoholic solution benzoate of potassa has a fatty aspect. It forms a difficultly soluble salt with excess of acid, in acicular crystals,  $= \text{KO}, 2\overline{\text{Bz}}$ , from which the redundant acid may be expelled by the cautious application of heat, so as to leave the neutral salt.

*Benzoate of Soda*,  $\text{NaO}, \overline{\text{Bz}}$ , crystallizes in efflorescent needles, difficultly soluble, even in boiling alcohol.

*Benzoate of Lime*,  $\text{CaO}, \overline{\text{Bz}}$ , forms acicular, plumose, and granular crystals, soluble in 20 parts of cold water, but much more soluble at  $212^\circ$ . When this salt is distilled, it yields *benzone*, together with *benzole* and *naphthaline*. *Benzone* is an oily colorless liquid, heavier than water. It differs from benzoic acid by 1 equivalent of carbonic acid, its formula being  $\text{C}_{13} \text{H}_5 \text{O}$ .

*Benzoate of Baryta*,  $\text{BaO}, \overline{\text{Bz}}$ , crystallizes in needles, permanent in the air, and difficultly soluble in cold water.

*Benzoate of Magnesia* in form resembles the lime salt; it requires 20 parts of cold water for solution.

*Benzoate of Manganese*,  $\text{MnO}, \overline{\text{Bz}}$ , forms permanent acicular crystals, soluble in 20 parts of cold water, and sparingly soluble in alcohol.

*Benzoates of Iron*. The *benzoate of the protoxide*,  $\text{FeO}, \overline{\text{Bz}}$ , crystallizes in efflorescent needles soluble in water and in alcohol.

The *benzoate of the peroxide*,  $\text{Fe}_2 \text{O}_3, 3\overline{\text{Bz}}$ , forms yellowish crystals, which, when dissolved either in water or in alcohol, leave a *basic* salt. There are two of these *basic benzoates*. The first is obtained by precipitating a solution of perchloride of iron, (to which alkali has been added so as just to render it yellow,) by a neutral benzoate of an alkali; the precipitate is reddish white, very bulky, insoluble in the saline liquid, but, when washed upon a filter, becomes more red, while the filtered liquor contains an acid salt: it may be washed without decomposition, first by an aqueous, and then by an alcoholic solution of sal ammoniac. The second basic salt is obtained when the solution of the perchloride is mixed, previous to precipitation, with a sufficient quantity of caustic ammonia to render it deep red: it is also formed when the mixture in which the first salt is precipitated, is boiled for some time: this salt is not decomposed by washing; it contains 25 *per cent.* of oxide of iron. In analysing ferriferous minerals, an alkaline benzoate is sometimes used to throw down the iron, but it is not admissible when certain of the earths proper are present.

*Benzoate of Zinc*.  $\text{ZnO}, \overline{\text{Bz}}$ . When solutions of benzoate of ammonia and sulphate of zinc are mixed, a white precipitate falls, soluble in excess of ammonia. This compound has not been adequately examined.

*Benzoates of Tin*,  $\text{SnO}, \overline{\text{Bz}}$ , and  $\text{Sn O}_2, 2\overline{\text{Bz}}$ , are white precipitates formed by double decomposition.

*Benzoate of Cobalt*,  $\text{CoO}, \overline{\text{Bz}}$ , is a red crystallizable salt.

*Benzoate of Nickel*,  $\text{NiO}, \overline{\text{Bz}}$ , is a green soluble and crystallizable salt. *Basic salts* may be obtained by boiling the hydrated oxides of cobalt and of nickel in a solution of the neutral benzoate.

*Benzoate of Copper*,  $\text{CuO}, \overline{\text{Bz}}$ , formed by double decomposition, is a difficultly soluble blue precipitate, which becomes green on drying; it may be obtained in crystals from its solution in warm dilute acetic acid.

*Benzoate of Lead*,  $\text{PbO}, \overline{\text{Bz}}$ , falls as a white crystalline powder, when formed by double decomposition; it is soluble in hot dilute acetic acid, and is deposited in crystalline scales as the solution cools. It contains 1 atom of water,  $= 3.79$  per cent., which it loses when dried at  $212^\circ$ . A *tribasic benzoate of lead*,  $= 3\text{PbO}, \overline{\text{Bz}}$ , falls in the form of an anhydrous white powder, when a solution of subacetate of lead is precipitated by benzoate of potassa.

*Benzoate of Bismuth*,  $\text{BiO}_3, 3\overline{\text{Bz}}$ , is a white precipitate, soluble, according to Trommsdorff, in a hot solution of benzoic acid, which on cooling deposits acicular crystals, soluble in water and in alcohol, with a slight residue of the oxide.

*Benzoate of Mercury*,  $\text{Hg}_2\text{O}, \overline{\text{Bz}}$ , is a white, curdy, or occasionally crystalline precipitate, soluble to a certain extent in excess of benzoic acid. When cautiously heated it may be sublimed. Ammonia converts it into a black powder, which, according to Harff, is  $\text{Hg}_2\text{O}, \overline{\text{Bz}} + \text{NH}_3$ . The benzoate of the red oxide,  $\text{HgO}, \overline{\text{Bz}}$ , is formed by heating a mixture of the oxide and the acid with water; it is a difficultly soluble white powder, which, according to Trommsdorff, may be sublimed in plumose crystals. With ammonia it forms a white basic compound.

*Benzoate of Silver*,  $\text{AgO}, \overline{\text{Bz}}$ , is a white curdy precipitate when formed by double decomposition, which dissolves in boiling water, and falls in crystalline scales as the solution cools. It is anhydrous. Exposed to light it becomes brown.

*Benzoate of Gold* and *Benzoate of Platinum* are formed when the oxides of those metals, thrown down by potassa, are dissolved in a boiling mixture of benzoic acid and water. Yellow crystals are obtained which are difficultly soluble in water and insoluble in alcohol. They are probably double salts. Benzoate of soda forms no precipitate in solutions of gold or of platinum.

*Benzoate of Palladium*,  $\text{PdO}, \overline{\text{Bz}}$ , is a white precipitate, soluble in a large quantity of water.

*Benzoate of Alumina*,  $\text{Al}_2\text{O}_3, 3\overline{\text{Bz}}$ , forms a crystalline mass, tolerably soluble in water, although it is precipitated when benzoate of potassa is added to a concentrated solution of a salt of alumina.

**ACTION OF CHLORINE AND BROMINE ON BENZOIC ACID.** *Chlorobenzoic Acids*. When benzoic acid is subjected to the action of dry chlorine, under the influence of the sun's rays, hydrochloric acid is generated, and a tough reddish viscid mass is produced, which, when digested in a solution of carbonated alkali, produces effervescence, and an acid substance combines with the alkali, whilst a chlorinated resin remains undissolved. If the alkaline solution be neutralized by hydrochloric acid, a precipitate somewhat resem-



bling benzoic acid, but which contains chlorine, falls; it is fusible at  $208^{\circ}$ , and soluble in boiling water, which, on cooling, deposits it in crystals resembling those of benzoic acid, and soluble in alcohol and in ether; with the bases it produces peculiar salts, which when burned, leave compounds of chlorine. Stenhouse has pointed out the resemblances between this acid and the benzoic, like which it may be sublimed; it does not precipitate nitrate of silver unless previously combined with a base, and the precipitate then formed resembles benzoate of silver, only it is less soluble in boiling water. Stenhouse found, that of the 5 atoms of hydrogen belonging to the anhydrous benzoic acid, not more than 3 could be replaced by chlorine, but that there are three distinct *chlorobenzoic acids*, represented by the following formulæ:

1. =  $C_{14} H_4 O_3 Cl$
2. =  $C_{14} H_3 O_3 Cl_2$
3. =  $C_{14} H_2 O_3 Cl_3$

These acids, however, so closely resemble each other, that they can only be distinguished by quantitative analysis.

*The relations of bromine and benzoic acid* resemble, according to Herzog, those of chlorine. Peligot (*Ann. der Pharm.*, xi. 277) found, that on passing the vapor of bromine slowly over benzoate of silver, a *bromobenzoic acid* and hydrobromic acid were formed; on digesting the product in alcohol, and suffering the solution spontaneously to evaporate, crystallized bromobenzoic acid was obtained,  $= C_{28} H_9 O_8, Br + 2HO$ . This substance fuses at  $212^{\circ}$ , and sublimes at  $482^{\circ}$ ; it is little soluble in water, but abundantly in alcohol and ether. It is *bibasic*, forming soluble salts with lime, baryta, and the oxides of copper, lead, and silver.

**ACTION OF SULPHURIC ACID ON BENZOIC ACID.** *Sulphobenzoic Acid.* *Hyposulphobenzoic Acid.* At common temperature benzoic acid dissolves in sulphuric acid, and on adding water it again separates; a small portion however always remains in combination, the quantity of which increases in proportion to the time they are left together. The compound is best obtained by Mitscherlich's process, which consists in gradually mixing benzoic acid with half its weight of anhydrous sulphuric acid; the combination takes place with the evolution of heat, and forms a thick transparent mass, which, when dissolved in water, deposits the excess of benzoic acid. When this solution is saturated by carbonate of baryta, sulphate of baryta falls, and a soluble salt is retained, the solution of which is filtered off, concentrated by evaporation, and mixed whilst warm with a quantity of hydrochloric acid sufficient to saturate half of the dissolved baryta; on cooling, a barytic salt is deposited, which requires to be redissolved and recrystallized. When thus purified, its solution is accurately decomposed by sulphuric acid, and filtered; the clear liquor, which is a solution of the *sulphobenzoic acid*, is then concentrated by evaporation till it sustains a temperature of  $300^{\circ}$  without boiling; it then concretes on cooling into a crystalline mass. It may be heated above  $300^{\circ}$  without decomposition, but the exact temperature at which this ensues has not been determined. This acid is not decomposed by boiling with nitric acid. Its affinities exceed those of most of the vegetable acids; it occasions a precipitate of acid *sulphobenzoate of*

*baryta* in the solution of nitrate of baryta and of chloride of barium. Mitscherlich concluded that this acid consisted of a combination of 2 atoms of sulphuric with 1 of benzoic acid; but Fehling has shown (*Ann. der Pharm.*) that in its production, the benzoic acid loses 2 atoms of hydrogen, and that the 2 atoms of sulphuric acid lose 1 atom of oxygen; so that the benzoic acid becomes  $C_{14}H_4O_3$ , and the 2 atoms of sulphuric acid become 1 atom of hyposulphuric acid  $=S_2O_5$ ; the sulphobenzoic acid therefore is  $C_{14}H_4O_3 + S_2O_5 + 2HO$ . Berzelius has shown that another view of the constitution of this acid may be supported, which represents it as  $C_{14}H_4O_2 + 2[SO_3, HO]$ , and that when 1 atom of its water is replaced by a fixed base, it forms *acid* salts, and *neutral* salts when both atoms are so replaced. (*Lehrbuch*, iv. 324.) In this case then, the *anhydrous* sulphobenzoic acid would be  $=C_{14}H_4O_2, 2SO_3$ . In either case, the equivalent of the acid, as the following table shows, would be 184.

| Berzelius.                          |    |     |     |           | Fehling.           |    |     |     |           |
|-------------------------------------|----|-----|-----|-----------|--------------------|----|-----|-----|-----------|
| Carbon .....                        | 14 | ... | 84  | ... 45·65 | Carbon .....       | 14 | ... | 84  | ... 45·65 |
| Hydrogen .....                      | 4  | ... | 4   | ... 2·17  | Hydrogen .....     | 4  | ... | 4   | ... 2·17  |
| Oxygen .....                        | 2  | ... | 16  | ... 8·69  | Oxygen .....       | 3  | ... | 24  | ... 13·04 |
| Sulphuric acid...                   | 2  | ... | 80  | ... 43·49 | Hyposulphuric acid | 1  | ... | 72  | ... 39·14 |
| <hr/>                               |    |     |     |           |                    |    |     |     |           |
| Anhydrous sul-<br>phobenzoic acid } | 1  |     | 184 | 100·00    |                    | 1  |     | 184 | 100·00    |

*Sulphobenzoates.* The sulphobenzoic acid saturates *two* atoms of bases, of which *one* may be replaced by water. The salts of lime, strontia, and lead, may be obtained directly; the others, by double decomposition. The acid salts of potassa and of soda, and of the oxides of iron, copper, cobalt, and manganese, may, according to Mitscherlich, be obtained in fine crystals. The neutral potassa-salt is also crystallizable, but deliquescent.

*Sulphobenzoates of Baryta.* The *neutral salt* is represented by Fehling as  $2BaO, + C_{14}H_4O_3, S_2O_5$ . It is formed by boiling carbonate of baryta with the acid, and is deposited in small crystals as the liquor cools. It consists of

|  |    |     |     |     |        |     | Fehling. | Mitscherlich. |
|--|----|-----|-----|-----|--------|-----|----------|---------------|
| Carbon .....                               | 14 | ... | 84  | ... | 24.85  | ... | 25.261   | } 56.32       |
| Hydrogen .....                             | 4  | ... | 4   | ... | 1.18   | ... | 1.178    |               |
| Oxygen .....                               | 3  | ... | 24  | ... | 7.10   | ... | 7.084    |               |
| Hyposulphuric acid                         | 1  | ... | 72  | ... | 21.30  | ... | 21.300   |               |
| Baryta .....                               | 2  | ... | 154 | ... | 45.57  | ... | 45.177   | 43.68         |
| <hr/>                                      |    |     |     |     |        |     |          |               |
| Neutralsulphoben-<br>zoate of Baryta ....} | 1  |     | 338 |     | 100.00 |     | 100.000  | 100.00        |

The *acid salt*,  $BaO, HO, + C_{14}H_4O_3, S_2O_5$ , is obtained as described for the preparation of the acid; it crystallizes in modifications of an oblique rhombic prism. Mitscherlich represents it as  $BaO + C_{14}H_5O_3, 2SO_3$ .

*Sulphobenzoate of Lead.*  $2PbO + C_{14}H_4O_3, S_2O_5$ . This salt forms small groups of radiating acicular crystals, somewhat resembling *Wavellite*. They include 4 atoms of water; but when dried at  $430^\circ$ , become anhydrous, and consist of



|                                  |    |      |     |      |        | Fehling.    |
|----------------------------------|----|------|-----|------|--------|-------------|
| Carbon .....                     | 14 | .... | 84  | .... | 20.59  | .... 20.700 |
| Hydrogen .....                   | 4  | .... | 4   | .... | 0.98   | .... 0.981  |
| Oxygen .....                     | 3  | .... | 24  | .... | 5.88   | .... 6.004  |
| Hyposulphuric acid .....         | 1  | .... | 72  | .... | 17.64  | .... 17.677 |
| Oxide of lead .....              | 2  | .... | 224 | .... | 54.91  | .... 54.638 |
| <hr/>                            |    |      |     |      |        |             |
| Anhydrous sulphobenzoate of lead | 1  |      | 408 |      | 100.00 | 100.000     |

*Sulphobenzoate of Silver* is formed by dissolving carbonate of silver in the acid, and evaporating *in vacuo*; it forms small yellow crystals, containing 4.2 per cent. of water of crystallization, the formula of which is  $2\text{AgO} + \text{C}_{14}\text{H}_4\text{O}_3, \text{S}_2\text{O}_5 + 2\text{HO}$ .

**ACTION OF NITRIC ACID ON BENZOIC ACID.** *Nitrobenzoic Acid.* This acid is obtained by boiling benzoic acid for several hours in concentrated nitric acid, till nitrous gas is no longer evolved, and the liquor has become colorless. The new acid separates on cooling, and must be purified by repeated solutions in boiling water and recrystallization. It then forms a colorless crystalline substance difficultly-soluble in cold, but abundantly in hot water, when, if the acid be in excess, it separates in a form resembling a heavy oil, which concretes on cooling. It is readily soluble in alcohol and in ether. This acid may be dried at  $212^\circ$  without loss of weight. It fuses at  $260^\circ$ , and gradually sublimes, leaving, if pure, no residue. The sublimed acid is white and crystalline, and its vapor very irritating: it dissolves, without decomposition, in hydrochloric and in nitric acid; it may be sublimed unchanged in chlorine. When its solution in sulphuric acid is gently heated, the acid sublimes, but at a higher temperature the liquid reddens, no gas is evolved, and if it then be diluted, unchanged acid falls in the form of a grey flocculent precipitate, the liquor still remaining of a red color, and when saturated by carbonate of baryta, yielding crystals of a compound not as yet examined. Mulder's formula for this acid in its crystalline form, is  $\text{HO} + \text{C}_{14}\text{H}_4\text{O}_3, \text{NO}_4$ ; its elements are

|                                |    |      |     |      |        | Mulder.    | Marchand. |
|--------------------------------|----|------|-----|------|--------|------------|-----------|
| Carbon .....                   | 14 | .... | 84  | .... | 50.29  | .... 51.02 | .... 50.9 |
| Hydrogen .....                 | 5  | .... | 5   | .... | 2.99   | .... 2.99  | .... 2.9  |
| Oxygen .....                   | 8  | .... | 64  | .... | 38.35  | .... 37.55 | .... 37.6 |
| Nitrogen .....                 | 1  | .... | 14  | .... | 8.37   | .... 8.44  | .... 8.6  |
| <hr/>                          |    |      |     |      |        |            |           |
| Crystallised nitrobenzoic acid | 1  |      | 167 |      | 100.00 | 100.00     | 100.0     |

*Nitrobenzoates.* These salts are for the most part crystallizable, and soluble in water and in alcohol. They deflagrate when heated, but when subjected to careful distillation yield *nitrobenzide*.

*Nitrobenzoate of Baryta*,  $\text{BaO}, \text{C}_{14}\text{H}_4\text{O}_3, \text{NO}_4 + 4\text{HO}$ , forms brilliant crystals, which effloresce, and lose their water of crystallization at  $212^\circ$ .

*Nitrobenzoate of Lead.*  $\text{PbO}, \text{C}_{14}\text{H}_4\text{O}_3, \text{NO}_4$ . When basic acetate of lead is added to a boiling saturated solution of nitrobenzoic acid, the first formed precipitate redissolves; but on continuing the addition of the solution of lead till the precipitate remains, the whole liquor concretes, on cooling, into a crystalline mass, which cannot be redissolved. When nitrobenzoate of lead is formed by double decomposition, the salt which falls consists of a compound of 1 atom of oxide of lead with 5 atoms of the neutral salt.

*Nitrobenzoate of Silver*,  $\text{AgO}$ ,  $\text{C}_{14}\text{H}_4\text{O}_3$ ,  $\text{NO}_4$ , is obtained by precipitating a solution of nitrate of silver with nitrobenzoate of ammonia. It is sparingly soluble in water, and separates in small crystals during the cooling of its boiling aqueous solution. At  $212^\circ$  this salt parts with a little of its acid: subjected to distillation at  $392^\circ$ , it yields a large proportion of *nitrobenzide*, which may be purified by distillation over carbonate of lime.

**BENZAMIC ACID.**  $\text{HO}$ ,  $\text{NH}_2$ ,  $\text{C}_{14}\text{H}_4\text{O}_3$ . This compound was discovered by Zinin (*Erdmann and Marchand's Journ.*, xxxv. 103;) it is the result of the action of sulphuretted hydrogen upon nitrobenzoic acid. It is obtained by saturating an alcoholic solution of nitrobenzoic acid, first with ammonia, and then with sulphuretted hydrogen, and boiling the liquor for some time in a retort: it first becomes green, and then yellow, from the precipitation of sulphur, which is to be separated; the distillation is then to be continued, when alcohol and sulphuret of ammonia pass over. This distillate is then saturated with sulphuretted hydrogen, and returned into the retort, when the distillation is resumed; this operation may be repeated several times before the conversion of the nitrobenzoic acid is complete, which is indicated by the cessation of the deposition of sulphur. The liquor is then mixed with water, and boiled, to expel the sulphuretted hydrogen and alcohol, and evaporated to the consistence of syrup: it is now a solution of *benzamate of ammonia*, and is to be decomposed by excess of acetic acid, when in consequence of the separation of the benzoic acid, the mixture congeals into a yellow magma; this is suffered to drain, and is then dissolved in boiling water, decolorized by animal charcoal, and filtered whilst boiling hot; on cooling it deposits the *benzoic acid* in tufts of acicular crystals.

Benzoic acid has a sweetish sour taste; when heated, it fuses into a clear colorless liquid, and at a higher temperature partly sublimes and is partly decomposed. It is sparingly soluble in cold water, but much more soluble in boiling water, and in alcohol and ether. In all these solutions it has a tendency to absorb oxygen from the atmosphere, which converts it into a brown resinoid substance. It reddens litmus, and displaces carbonic acid. Pure nitric acid has no effect upon it, but the fuming acid dissolves it, forming a red liquor. It is readily decomposed by chlorine. With the alkalis and earths it forms uncrystallizable and very soluble salts. It combines in three proportions with oxide of lead, forming (1,) a pulverulent and almost insoluble compound; (2,) a difficultly-soluble salt in acicular crystals; (3,) a very soluble salt which crystallizes in scales. With oxide of copper it forms a malachite-green insoluble compound. With oxide of silver it also forms an insoluble combination, which is curdy when first precipitated, but soon forms a crystalline powder; it is rendered brown, but not dissolved, by boiling water.

Benzoic acid consists of

|                           |    |     |     |     | Zinin. |        |
|---------------------------|----|-----|-----|-----|--------|--------|
| Carbon .....              | 14 | ... | 84  | ... | 61.31  | 61.02  |
| Hydrogen.....             | 7  | ... | 7   | ... | 5.11   | 5.12   |
| Oxygen .....              | 4  | ... | 32  | ... | 23.36  | 23.85  |
| Nitrogen .....            | 1  | ... | 14  | ... | 10.22  | 10.01  |
| <hr/>                     |    |     |     |     |        |        |
| Crystallized benzoic acid | 1  |     | 137 |     | 100.00 | 100.00 |



The salt of silver afforded

|                     |    |      |     |      |        | Zinn.        |
|---------------------|----|------|-----|------|--------|--------------|
| Carbon .....        | 14 | .... | 84  | .... | 34.43  | .... 34.19   |
| Hydrogen .....      | 6  | .... | 6   | .... | 2.46   | .... 2.54    |
| Oxygen .....        | 4  | .... | 32  | .... | 13.11  | } .... 19.07 |
| Nitrogen .....      | 1  | .... | 14  | .... | 5.73   |              |
| Silver.....         | 1  | .... | 108 | .... | 44.27  | .... 44.20   |
| <hr/>               |    |      |     |      |        |              |
| Benzamate of Silver | 1  |      | 244 |      | 100.00 | 100.00       |

BENZOIC OXIDE. OXIDE OF BENZULE.  $C_{14}H_5O_2$ . This compound was discovered by Ettling, (*Ann. der Pharm.*, liii. 87,) and was afterwards more fully investigated by Stenhouse. (*ibid*, liii. 91, and lx. 10.) It may be regarded as derived from benzoic acid by the abstraction of an atom of oxygen; or, as the *radical* of benzoic acid. The term *benzoyle* or *benzule* has sometimes therefore been applied to it, or at least to an isomeric compound; but that term ought rather to be reserved for the hydrocarbon (as yet hypothetical,)  $C_{14}H_5$ , which, in combination with oxygen, forms both benzoic oxide and benzoic acid.

Benzoic oxide is obtained by heating *benzoate of copper* in a retort to which a cold receiver is attached; a liquid distils over which concretes into crystalline drops consisting of benzoic oxide and benzoic acid; this is subjected to pressure between folds of blotting paper, and then digested in repeated portions of a hot solution of carbonate of soda, which removes the benzoic acid; the remaining benzoic oxide is then washed with water, dried, and purified by repeated solution and crystallization in alcohol or ether. It forms oblique four-sided prisms, which are hard and brittle, fusible at  $160^\circ$ , and of an agreeable lemon odor. They consist of

|               |    |      |     |      |        | Stenhouse. | Ettling.   |
|---------------|----|------|-----|------|--------|------------|------------|
| Carbon .....  | 14 | .... | 84  | .... | 80.00  | .... 80.01 | .... 79.16 |
| Hydrogen..... | 5  | .... | 5   | .... | 4.76   | .... 5.18  | .... 5.11  |
| Oxygen.....   | 2  | .... | 16  | .... | 15.24  | .... 14.81 | .... 15.73 |
| <hr/>         |    |      |     |      |        |            |            |
| Benzoic oxide | 1  |      | 105 |      | 100.00 | 100.00     | 100.00     |

When benzoic oxide is boiled in a solution of potassa, it gradually absorbs oxygen from the air, and passing into benzoic acid, benzoate of potassa is formed in the liquor. If the solution of potassa be very strong, or if benzoic oxide be fused with hydrate of potassa, hydrogen is evolved, and benzoic acid formed in consequence of the decomposition of water. When chlorine is passed for some days over fused benzoic oxide, a soft yellow compound is produced, of an unpleasant acrid odor; it concretes at  $32^\circ$ . When the more fluid part is removed by pressure between folds of blotting paper, and the remaining solid purified by solution and crystallization in ether, it forms flat crystals, of a peculiar odor, and fusible at  $185^\circ$ ; they may be volatilized by heat, and condense in a prismatic form: their formula, according to the analysis of Stenhouse, is  $C_{75}H_{27}O_{10}Cl_3$ .

BENZAMIDE. This substance was discovered by Wöhler and Liebig, in 1832. It may be represented as an *amide of benzoic oxide*, by the rational formula  $NH_2 + C_{14}H_5O_2$ . It is formed (simultaneously with sal ammoniac) by the action of dry ammonia on chloride of benzoic

oxide; the sal-ammoniac is removed by cold water, and the remaining benzamide dissolved in boiling water, which deposits it in crystals on cooling. Benzamide is also formed, according to Fehling, by boiling peroxide of lead in a solution of *hippuric acid*: (p. 1374.) It forms pearly crystals resembling those of chlorate of potassa, when its hot solution is quickly cooled; but if very gradually cooled, it concretes into a congeries of silky crystals; but these gradually change their aspect and produce large iridescent prisms, which are sometimes flattened into a tabular form, and which appear greasy when put into water. Benzamide fuses at  $240^{\circ}$ , and solidifies on cooling into a crystalline mass; at higher temperatures it boils, and distils over unchanged, its vapor having the odor of bitter almond oil. It is almost insoluble in cold water, but readily soluble in alcohol and in ether. When benzamide is heated with excess of caustic baryta, ammonia is evolved, and a colorless oil distils over. The same product is obtained, without the evolution of ammonia, by the action of potassium, cyanide of potassium being at the same time formed. The oil is colorless, lighter than water, of an aromatic odor and sweet taste; it is not altered by concentrated acids or alkalis, and potassium may be fused in it without effect.

The ultimate components of benzamide are

|                      |         |      |           |      | Liebig and Wöhler. |               | Fehling.     |
|----------------------|---------|------|-----------|------|--------------------|---------------|--------------|
| Carbon .....         | 14      | .... | 84        | .... | 69.42              | ....          | 69.92        |
| Hydrogen .....       | 7       | .... | 7         | .... | 5.79               | ....          | 5.84         |
| Oxygen .....         | 2       | .... | 16        | .... | 13.22              | ....          | 13.22        |
| Nitrogen .....       | 1       | .... | 14        | .... | 11.57              | ....          | 11.02        |
| <hr/> Benzamide .... | <hr/> 1 |      | <hr/> 121 |      | <hr/> 100.00       | <hr/> 100.000 | <hr/> 100.00 |

*Bromide of Benzamide* is formed by dissolving benzamide in bromine; after about 14 days, red crystals are formed, composed of 1 atom of benzamide + 2 atoms of bromine. (LAURENT.) They are slowly decomposed by water, and suddenly by ammonia, which separates benzamide.

HYDRURET OF OXIDE OF BENZOYLE.  $C_{14}H_5O_2 + H$ , or  $C_{14}H_6O_2$ . *Hydruret of Benzule. Oxide of Picramyle. Oxide of Stilbene.* These terms have been applied to the well-known product of the distillation of bitter almonds, commonly called *bitter almond oil*. This compound, as Liebig and Wöhler first demonstrated, does not exist ready formed in the bitter almond, but is the product of the action of emulsine (p. 1233,) upon *amygdaline*, (p. 1375.)

Bitter almond oil is obtained by macerating the pulverized bitter almond cake, after the fixed oil has been expressed, in water heated to about  $100^{\circ}$ , for 24 hours, and then distilling; it passes over along with the vapor of water, and condenses in the receiver in the form of a heavy oil, the supernatant water holding a portion of it in solution: (*Aqua Amygdal. amar.* of pharmacy\*.) This oil is combined with hydrocyanic

\* Dr. Gregory has the following remarks upon the *distilled water of bitter almonds*. "Expressed bitter almonds are made into a thin cream with water, and this distilled in the heat of a chloride of calcium bath

till a quantity of water has passed over equal in weight to the almonds before being pressed. The distilled water is milky from suspended oil of bitter almonds, and smells both of hydruret of benzoyle and of hydro-



acid, and is therefore, as well as the bitter almond water, very poisonous. It may be obtained also from peach and apricot kernels, from the leaves of the laurel (*Prunus laurocerasus*), and from the bark of the wild cherry, (*Prunus padus*.) To free it from hydrocyanic acid, the oil may be mixed and thoroughly agitated with milk of lime and a solution of protochloride of iron, and on distilling this mixture, the oil passes over in a comparatively pure state; but the process generally requires repetition before the whole of the hydrocyanic acid is abstracted, and even then, the purified oil must be rectified over quicklime to deprive it of water and benzoic acid. According to Grindlay (*Pharm. Journ.*, vii. 11,) the crude oil of bitter almonds is more effectively purified by mixing it with an equal quantity of water, and then digesting it in a water-bath with red oxide of mercury, and small quantities of lime and of protochloride of iron; and having allowed time for the decomposition of the hydrocyanic acid, subjecting the mixture to distillation; pure hydruret of benzule then passes over, and cyanide of mercury, benzoate of lime, chloride of calcium, and oxide of iron, remain in the retort, together with some *benzoin*e, and any excess of the ingredients employed. A copper retort is recommended to be used, in consequence of the bumpings which ensue, and which endanger a vessel of glass.

Pure bitter almond oil is a colorless liquid of a peculiar and agreeable aromatic odor and a pungent flavor. It is not poisonous when entirely free from hydrocyanic contamination; and as it is much used in confectionery and cookery, great care should be taken that for such purposes its purification has been adequately performed. Its boiling-point is about 350°. It is easily inflammable, and burns with a bright sooty flame. It is soluble in about 30 parts of water, and in all proportions in alcohol and ether. Its alcoholic solution constitutes the *Essence of bitter almonds* commonly sold for culinary purposes; it usually consists of 1 part of the oil dissolved in 7 of alcohol. This oil is also soluble without decomposition in sulphuric and nitric acid. Its components are

|                        |    |      |     |      |        | Liebig and Wöhler. |        |             |
|------------------------|----|------|-----|------|--------|--------------------|--------|-------------|
| Carbon .....           | 14 | .... | 84  | .... | 79.25  | ....               | 79.44  | .... 79.603 |
| Hydrogen .....         | 6  | .... | 6   | .... | 5.66   | ....               | 5.75   | .... 5.734  |
| Oxygen .....           | 2  | .... | 16  | .... | 15.09  | ....               | 14.81  | .... 14.663 |
| <hr/>                  |    |      |     |      |        |                    |        |             |
| Bitter almond oil .... | 1  |      | 106 |      | 100.00 |                    | 100.00 | 100.000     |

cyanic acid. When freshly prepared it contains little more than 1 grain of hydrocyanic acid per ounce; but its strength diminishes by keeping, and as it is difficult to obtain it of uniform strength even when fresh, it is not a good form of administering hydrocyanic acid. It is remarkable that nitrate of silver does not detect the hydrocyanic acid unless ammonia is added with the nitrate, and after a time neutralized by nitric acid. It is used in medicine, especially on the Continent, and is poisonous." "*Laurel water* is obtained by distilling 2 parts of fresh leaves of *Prunus laurocerasus* with water, till 3 parts have passed over. It exactly resembles the pre-

ceding water, and is equally uncertain and equally poisonous." (*Outlines*, p. 341.) Liebig has lately suggested the use of sulphuret of ammonium with excess of sulphur for detecting hydrocyanic acid, and it is extremely delicate when properly applied, its action depending upon the formation of sulphocyanide of ammonium, and the ready detection of the latter by its reddening the persalts of iron. (*Chem. Gaz.*, 1847, p. 143.) A. Taylor has shown that this test may be successfully employed when the other tests for hydrocyanic acid are unavailable. (*Medical Gazette*, April, 1847.)

By the protracted action of dry chlorine on pure bitter almond oil hydrochloric acid is evolved, and a compound is formed, which has been termed *chloride* or *oxychloride of benzoyle*; it is a colorless liquid of the sp. gr. 1.196: it has a peculiar penetrating odor somewhat analogous to that of horse-radish. By the action of hot water it is resolved into hydrochloric and benzoic acid; its formula is  $C_{14}H_5O_2Cl$ , so that in its formation, an atom of the hydrogen of the oil is replaced by an atom of chlorine. When bromine is made to act in the same way upon bitter almond oil, hydrobromic acid is evolved, and an *oxybromide of benzule* is formed,  $[C_{14}H_6O_2 + 2Br = C_{14}H_5O_2, Br + HBr.]$  It is a semifluid crystalline substance, less pungent than the chloride, and of a somewhat aromatic odor; it is soluble in alcohol and ether, and when long boiled with water, yields benzoic and hydrobromic acid. *Oxyiodide of benzule* is formed when the oxychloride is heated with iodide of potassium; a brown liquid distils over, which concretes on cooling into a brown crystalline substance. When deprived of excess of iodine it is colorless; in other respects it resembles the oxybromide.

*Sulphuret of Oxide of Benzoyle*,  $C_{14}H_6O_2S$ , is produced by distilling the oxychloride off finely-pulverized sulphuret of lead; it passes over in the form of a yellow oil, which concretes on cooling into a yellow crystalline mass, of a disagreeable odor, and not decomposed by boiling water. When heated in an aqueous solution of potassa, sulphuret of potassium and benzoate of potassa are slowly formed. *Cyanide of benzoyle* is a liquid having an odor like that of cinnamon.

*Hydruret of Sulphobenzoyle*,  $C_{14}H_5S_2 + H$ . (*Schwefel Picramyle*. LÖWIG.) When 1 volume of crude bitter almond oil is dissolved in 8 of alcohol and gradually mixed with 1 volume of sulphuret of ammonium, a fine granular white powder is gradually deposited, which gives to the fingers a persistent order of garlic; it is insoluble in water and in alcohol. Ether liquefies it, but a few drops of alcohol restore its solid form. It may be considered as the hydruret of a new radical, in which the oxygen of benzoic oxide has been replaced by sulphur. When heated it melts, and on cooling forms a plastic mass, which afterwards concretes into a brittle substance. When kept for some time in fusion it sustains a change, and then crystallizes on cooling. (LAURENT, *Ann. Ch. et Ph.*, 3ème Ser., i. 111.)

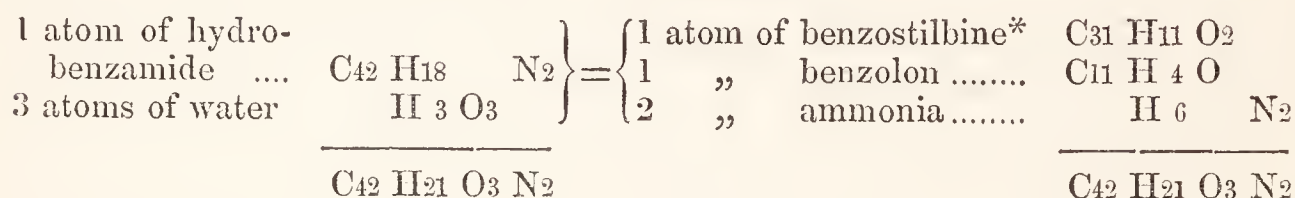
*Hydrobenzamide*,  $C_{42}H_{18}N_2$ . (*Stickstoff Picramyl*. LÖWIG.) This compound was discovered by Laurent, (*Ann. Ch. et Ph.*, lxii. 23;) it has been examined by Liebig, (*Ann. der Pharm.*, xxv. 25,) Rochleder, (*Ibid.*, xli. 89,) and Fownes. (*Ibid.*, liv. 363.) It is formed by digesting a mixture of pure bitter almond oil, with a large quantity of strong solution of ammonia, in a well-stopped vessel, at a temperature between  $110^\circ$  and  $120^\circ$ . In a few days it is converted into a white crystalline product, which is to be washed with ether, and dissolved in warm alcohol; on cooling, and by spontaneous evaporation, the hydrobenzamide is deposited in regular octohedral crystals, colorless, tasteless, and inodorous, insoluble in water, but readily soluble in alcohol and in ether. The alcoholic solution tastes of burned almonds. This substance fuses at a little above  $212^\circ$  into a thick oil, which again slowly concretes. It is readily decomposed by heat, and when acted on by hydrochloric acid, or by ether, it is resolved into ammonia and bitter almond oil:  $C_{42}H_{18}N_2 + 6HO$



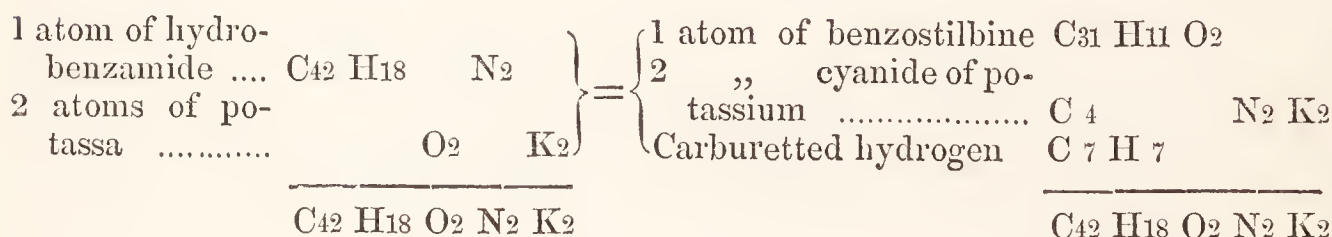
$= 3[\text{C}_{14} \text{H}_6 \text{O}_2] + 2[\text{NH}_3.]$  The following are the results of the analyses of hydrobenzamide :—

|                |    |      |     |      |        | Laurent. |         | Liebig. |        | Rochleder, |
|----------------|----|------|-----|------|--------|----------|---------|---------|--------|------------|
| Carbon .....   | 42 | .... | 252 | .... | 84.53  | ....     | 84.405  | ....    | 84.31  | .... 84.86 |
| Hydrogen.....  | 18 | .... | 18  | .... | 6.04   | ....     | 6.383   | ....    | 6.07   | .... 6.01  |
| Nitrogen ..... | 2  | .... | 28  | .... | 9.43   | ....     | 9.212   | ....    | 9.62   | .... 9.13  |
| Hydrobenzamide | 1  |      | 298 |      | 100.00 |          | 100.000 |         | 100.00 | 100.00     |

When hydrobenzamide is subjected to dry distillation, ammonia is first evolved, and then a thin, agreeably-smelling oil. As soon as the formation of ammonia ceases, a fused mass is found in the retort, which crystallizes on cooling, and contains two products, one of which is soluble in ether, and crystallizes in lamellar tables from its aqueous solution; the other is, according to Laurent, an organic basis (which he has termed *Lophine*)  $= \text{C}_{46} \text{H}_{17} \text{N}_2$ ; it is insoluble in ether. When hydrobenzamide is fused in a silver basin with pulverized hydrate of potassa, the mixture becomes yellow, and then nearly black, and evolves ammonia, and afterwards hydrogen and carburetted hydrogen. The residuary black substance, when washed with water, yields cyanide and carbonate of potassium, and leaves a yellow powder, which is a mixture of an oily matter with *benzostilbine* and *benzolon*. (ROCHLEDER.)



And again



When hydrobenzamide is boiled for some hours with solution of caustic potassa, a brown crystalline substance is formed, and a resin-like substance having basic characters, and isomeric with hydrobenzamide. Fownes terms this substance *benzoline*; according to Löwig, it is identical with *amarine*, discovered by Laurent.

When the *crude* bitter almond oil is subjected to the action of ammonia, an isomeric modification of hydrobenzamide is formed, which Laurent terms *Benzhydramide*, together with two other compounds, namely, *Azobenzoyle*,  $\text{C}_{42} \text{H}_{15} \text{N}_2$ , and *azotide of benzoyle*,  $\text{C}_{14} \text{N}_5 \text{N}$ , (or nitrobenzoyle?) *Azobenzoyle* is much less soluble in alcohol than *benzhydramide*, and is derived from oxide of benzoyle as follows:  $3[\text{C}_{14} \text{H}_5 \text{O}_2] + 2\text{NH}_3 = \text{C}_{42} \text{H}_{15} \text{N}_2 + 6\text{HO}$ . *Azotide of benzoyle* is insoluble in boiling alcohol, and is supposed to be derived from anhydrous benzoic acid and ammonia, as follows:  $\text{C}_{14} \text{H}_5 \text{O}_3 + \text{NH}_3 = \text{C}_{14} \text{H}_5 \text{N} + 3\text{HO}$ . (LIEBIG.)

*Benzimide*.  $\text{C}_{28} \text{H}_{11} \text{O}_4 \text{N}$ . This is a white, inodorous, shining crystal-

\* According to Löwig benzostilbine is  $\text{C}_{16} \text{H}_6 \text{O}$ .

line substance, occasionally formed in crude bitter almond oil; it is insoluble in water, and only slightly soluble in alcohol and ether. It is characterized by the dark blue color of its solution in oil of vitriol, which becomes green when diluted. (LAURENT.)

*Benzoïne.* There is a remarkable isomeric modification of bitter almond oil which has been termed *Benzoïne*, or *Bitter Almond Oil Camphor*, (LIEBIG and WÖHLER, *Poggend.*, xxvi. 474; *Ann. der Pharm.*, iii. 249.) It is formed, when crude bitter almond oil is mixed with its bulk of a freshly-prepared saturated solution of potassa in alcohol; in a few minutes the mixture concretes into a yellow crystalline mass composed of a mixture of benzoïne with a resinous matter, from which it may be freed by recrystallization from its alcoholic solution. Benzoïne is also formed by the action of a weak alcoholic solution of cyanide of potassium upon the crude bitter almond oil. (ZININ, *Ann. der Pharm.*, xxxiv. 108.)

Benzoïne forms brilliant white prismatic crystals, insipid and inodorous, fusible at  $250^{\circ}$  into a clear liquid, which concretes on cooling into a radiated lamellar mass, and at a higher temperature boils into vapor without decomposition. It is very inflammable, and burns with a bright but smoky flame. It is insoluble in cold, and almost insoluble in boiling water, but soluble in alcohol. Its formula is probably  $C_{28}H_{12}O_4 = 2[C_{14}H_6O_2]$ , so that its composition and equivalent will be

| Liebig and Wöhler. |    |     |     |     |        |     |         |
|--------------------|----|-----|-----|-----|--------|-----|---------|
| Carbon.....        | 28 | ... | 168 | ... | 79.28  | ... | 79.079  |
| Hydrogen           | 12 | ... | 12  | ... | 5.66   | ... | 5.688   |
| Oxygen ....        | 4  | ... | 32  | ... | 15.06  | ... | 15.233  |
| <hr/>              |    |     |     |     |        |     |         |
| Benzoïne....       | 1  |     | 212 |     | 100.00 |     | 100.000 |

When chlorine is passed over fused benzoïne, or when it is gently heated with concentrated nitric acid, it is converted into *benzile*  $= C_{28}H_{10}O_4$ ; a substance therefore isomeric with Wöhler's *benzule* (*Benzoic oxide*, or *oxide of Benzule*  $= C_{14}H_5O_2$ . See page 1364.) Benzoïne passes into *benzile* by the loss of 2 atoms of hydrogen; thus, in the case of its formation by chlorine,  $C_{28}H_{12}O_4 + Cl_2 = C_{28}H_{10}O_4 + 2HCl$ ; and when nitric acid is used,  $C_{28}H_{12}O_4 + 2NO_5 = C_{28}H_{10}O_4 + 2NO_4 + 2HO$ . (ZININ. LAURENT, *Ann. der Pharm.*, xvii. 91.)

*Benzile* is a concrete crystalline substance, which may be obtained in large prisms from its ethereal solution: it is tasteless, inodorous, insoluble in water, but very soluble in alcohol and in ether, and may be fused and sublimed without change. It has been analyzed with the following results:

| Laurent.      |    |     |     |     |        |     |         |
|---------------|----|-----|-----|-----|--------|-----|---------|
| Zinin.        |    |     |     |     |        |     |         |
| Carbon.....   | 28 | ... | 168 | ... | 80.00  | ... | 80.43   |
| Hydrogen .... | 10 | ... | 10  | ... | 4.76   | ... | 4.91    |
| Oxygen .....  | 4  | ... | 32  | ... | 15.24  | ... | 15.66   |
| <hr/>         |    |     |     |     |        |     |         |
| Benzile ..... | 1  |     | 210 |     | 100.00 |     | 100.000 |

When a hot alcoholic solution of benzile is mixed with an equal bulk of anhydrous hydrocyanic acid, a crystalline compound is formed  $= 2[C_{14}H_5O_2 + C_2NH]$ ; it is therefore a *hydrocyanate of benzile*.

When benzile is boiled in a recently-prepared and moderately strong solution of potassa, till the violet color at first produced has vanished,



and is no longer restored by a fresh portion of potassa, the liquor yields on evaporation in a water-bath, a saline mass, which, when exposed to air so as to convert any excess of potassa into carbonate, and then digested in alcohol, yields a solution of *benzilate of potassa*. This solution may be mixed with water and the alcohol distilled off, when an aqueous solution of the benzilate is obtained, which, after having been decolorized by animal charcoal, yields the crystallized salt on evaporation. When this benzilate of potassa is boiled in dilute hydrochloric acid, the filtered liquor gradually deposits benzilic acid.

*Benzilic acid* forms brilliant acicular crystals =  $C_{28}H_{11}O_5 + HO$ , difficultly soluble in cold water, but very soluble in alcohol and in ether; it is inodorous, and of a bitter, sour, and metallic taste; and fusible without loss of weight, at  $212^\circ$ . At higher temperatures it reddens, exhales a peculiar odor, and is decomposed with the evolution of a violet-colored vapor, which condenses into a crimson oily liquid, soluble in alcohol; its color is destroyed by the addition of ammonia or of potassa, and by nitric acid, but is not altered by hydrochloric or by sulphuric acid. Benzilic acid is soluble without decomposition in nitric acid: with sulphuric acid it produces a deep crimson color; with sulphuretted hydrogen it deposits sulphur, and forms an oily body having the odor of garlic.

*Benzilate of potassa* forms transparent crystals soluble both in water and in alcohol, but insoluble in ether, =  $KO, C_{28}H_{11}O_5$ . *Benzilate of lead*,  $PbO, C_{28}H_{11}O_5$ , is a white insoluble powder, fusible, and producing a violet vapor when heated up to its point of decomposition. *Benzilate of silver*,  $AgO, C_{28}H_{11}O_5$ , falls in the form of a white crystalline powder when nitrate of silver is decomposed by benzilate of potassa; it is very sparingly soluble in hot water; it acquires a blue tint when heated to  $212^\circ$ , but loses no weight; if, however, long retained at that temperature, it reddens, and begins to decompose; it is fusible, and gives off violet colored vapor at a high heat. (ZININ, *Ann. der Pharm.*, xxxi. 329.) Its components are

|                          |    |     |     |     |        | Zinin. |
|--------------------------|----|-----|-----|-----|--------|--------|
| Carbon .....             | 28 | ... | 168 | ... | 50.15  | 50.09  |
| Hydrogen .....           | 11 | ... | 11  | ... | 3.29   | 3.36   |
| Oxygen .....             | 5  | ... | 40  | ... | 11.94  | 11.57  |
| Oxide of silver .....    | 1  | ... | 116 | ... | 34.62  | 34.98  |
| <hr/>                    |    |     |     |     |        |        |
| Benzilate of silver..... | 1  |     | 335 |     | 100.00 | 100.00 |

*Mandelic Acid. Formobenzoilic Acid.*  $C_{16}H_7O_5 + HO$ . This compound was discovered by Winkler, (*Ann. der Pharm.*, xviii. 310,) and shown by Liebig to contain the elements of *formic acid* and *hydruret of benzoyl*; it is obtained by adding hydrochloric acid to a concentrated aqueous solution of crude bitter almond oil, and evaporating to dryness on a water-bath; the residue is a mixture of sal-ammoniac with benzamide and mandelic acid; the latter may be abstracted by ether, and purified by a second solution and evaporation.

Mandelic acid is in the form of a white crystalline powder, very sour, and having a slight bitter-almond odor. When carefully heated in a platinum crucible, it fuses into a yellow oily liquid, which, on cooling, concretes into a gum-like mass. At a high temperature it exhales a

benzoic odor, and is decomposed, leaving a bulky coal. If decomposed in close vessels, a brown balsamic product is obtained, containing bitter almond oil. It is soluble in water, alcohol, and ether; and when aided by heat decomposes the carbonates, acetates, and benzoates. When its aqueous solution is heated with peroxide of manganese, carbonic acid and bitter almond oil are formed; boiled with nitric acid, benzoic acid is formed. Chlorine produces an oily substance in the solution of mandelic acid, which has the odor of chloride of benzule, and on adding potassa, and then an acid, carbonic acid is evolved and benzoic acid precipitated. Mandelic acid consists of

|                                |    |     |     |     |        |     |         |
|--------------------------------|----|-----|-----|-----|--------|-----|---------|
|                                |    |     |     |     |        |     | Liebig. |
| Carbon.....                    | 16 | ... | 96  | ... | 63.15  | ... | 63.77   |
| Hydrogen .....                 | 8  | ... | 8   | ... | 5.27   | ... | 5.55    |
| Oxygen .....                   | 6  | ... | 48  | ... | 31.58  | ... | 30.68   |
| <hr/>                          |    |     |     |     |        |     |         |
| Crystallised mandelic acid.... | 1  |     | 152 |     | 100.00 |     | 100.00  |

The *mandelates* (or *formobenzoilates*) of *potassa* and of *soda*, are very soluble and difficultly crystallizable; the salt of *baryta* forms small transparent prisms, and that of *silver*, produced by the decomposition of nitrate of silver by mandelate of ammonia, is a white crystalline precipitate soluble in boiling water, which solution deposits lamellar and anhydrous crystals on cooling. (LIEBIG.)

*Benzoate of Hydruret of Benzule.*  $C_{42}H_{18}O_8$ . When moist chlorine is passed through the oil of bitter almonds, hydrated benzoic acid is formed, which, uniting with the unchanged oil, forms the above compound, containing 2 atoms of bitter almond oil with 1 of hydrated benzoic acid. When more water is present, benzoic and hydrochloric acids are the products.  $C_{14}H_6O_2 + HO + 2Cl = C_{14}H_5O_3 + 2HCl$ . This compound is either a pure white crystalline powder, or it forms short brilliant prisms, insoluble in water, soluble in alcohol, and very sparingly soluble in cold ether. It is abundantly soluble in alcohol saturated with hydrate of potassa, and the liquor gradually deposits crystals of benzoate of potassa. Its elements, according to Liebig, are

|                                |    |     |     |     |        |     |                    |
|--------------------------------|----|-----|-----|-----|--------|-----|--------------------|
|                                |    |     |     |     |        |     | Liebig.            |
| Carbon .....                   | 42 | ... | 252 | ... | 75.45  | ... | 75.805             |
| Hydrogen .....                 | 18 | ... | 18  | ... | 5.39   | ... | 5.304              |
| Oxygen .....                   | 8  | ... | 64  | ... | 19.16  | ... | 18.391             |
| <hr/>                          |    |     |     |     |        |     |                    |
| Benzoate of bitter almond oil} | 1  |     | 334 |     | 100.00 |     | 100.000            |
|                                |    |     |     |     |        |     | =                  |
|                                |    |     |     |     |        |     | { Hydrated {       |
|                                |    |     |     |     |        |     | { benzoic acid } 1 |
|                                |    |     |     |     |        |     | ...                |
|                                |    |     |     |     |        |     | 122                |
|                                |    |     |     |     |        |     | ...                |
|                                |    |     |     |     |        |     | 36.52              |
|                                |    |     |     |     |        |     | { Hydruret of {    |
|                                |    |     |     |     |        |     | { Benzoyle } 2     |
|                                |    |     |     |     |        |     | ...                |
|                                |    |     |     |     |        |     | 212                |
|                                |    |     |     |     |        |     | ...                |
|                                |    |     |     |     |        |     | 63.48              |
| <hr/>                          |    |     |     |     |        |     | <hr/>              |
|                                |    |     |     |     |        |     | 1                  |
|                                |    |     |     |     |        |     | 334                |
|                                |    |     |     |     |        |     | 100.00             |

When oil of bitter almonds is mixed with one-fourth its volume of dry hydrocyanic acid, and then warmed with its own volume of solution of potassa, sp. gr. 1.25, diluted with 6 parts of alcohol, a crystalline compound is formed, which has been termed *Hydrocyanate of Benzöine*; its formula is  $C_{46}H_{18}O_4N_2$ . It arises from the action of 3 atoms of hydruret of benzoyle upon 2 of hydrocyanic acid:  $3[C_{14}H_6O_2] + 2C_2NH = C_{46}H_{18}O_4N_2 + 2HO$ .

*Benzole.*  $C_{12}H_6$ . *Benzine.* *Benzène.* *Phène.* *Hydruret of Phenyle,* (p. 502). This is a hydrocarbon, isomeric with that discovered by Faraday in the products of the destructive distillation of oil. (See *Bicarburet of Hydrogen*, p. 483.) It is also said to be found amongst



the complicated products of the distillation of pit-coal. It is obtained, as already stated, (p. 1357,) by distilling benzoic acid with three times its weight of slaked lime. It is a limpid colorless liquid, of a pleasant odor, sp. gr. 0·85; it congeals at  $32^{\circ}$  and boils at  $186^{\circ}$ . In its production, 1 atom of benzoic acid is resolved into 2 of carbonic acid retained by the lime, and 1 of benzole.  $[C_{14}H_6O_4 = 2CO_2 + C_{12}H_6.]$

When acted upon by anhydrous sulphuric acid, benzole yields a viscid mass, which, when mixed with water, deposits a new compound, soluble in and crystallizable from ether, the formula of which is  $C_{12}H_5SO_2$ . This substance, which is quite neutral, has been termed *Sulphobenzide*. The solution retains an acid compound, the *hyposulphobenzidic acid*  $= C_{12}H_5S_2O_5 + HO$ . It may be regarded as resulting from the action of 2 atoms of anhydrous sulphuric acid upon 1 atom of benzole,  $[C_{12}H_6 + 2SO_3 = C_{12}H_5S_2O_5 + HO]$ ; or as a compound of sulphobenzide with oil of vitriol,  $= C_{12}H_5SO_2 + HO, SO_3$ . The pure acid is best obtained by decomposing the crystallized *hyposulphobenzidate of copper* by sulphuretted hydrogen. It crystallizes when evaporated to the consistence of syrup, and sustains a temperature of  $390^{\circ}$  without decomposition. It forms crystallizable salts. (MITSCHERLICH.)

*Nitrobenzide*,  $C_{12}H_5NO_4$ , is formed when benzole is dissolved to saturation in fuming nitric acid, and water added; as the liquor cools, nitrobenzide separates in the form of a heavy oil of a sweet taste and cinnamon odor; its sp. gr. is 1·209; it congeals at  $370$  and boils at  $434^{\circ}$ . It is insoluble in water, but soluble in alcohol and in ether. It is formed from 1 atom of benzole and 1 of nitric acid.  $C_{12}H_5 + NO_5 = C_{12}H_5NO_4 + HO$ .

When an alcoholic solution of nitrobenzide is distilled with dry hydrate of potassa, alcohol first passes over, and a new volatile and crystallizable compound, which has been distinguished by the term *azobenzide*, is formed; it is fusible at  $150^{\circ}$ , and boils at  $380^{\circ}$ . The formula assigned to this substance is  $C_{12}H_5N$ . Its production has not been explained. (MITSCHERLICH.)

*Chloride of Benzole*,  $C_{12}H_6Cl_6$ , is a crystalline solid, formed by the action of the sun's rays upon benzole in chlorine. When this compound is distilled with hydrate of lime, it yields *chlorobenzine*,  $= C_{12}H_3Cl_3$ .

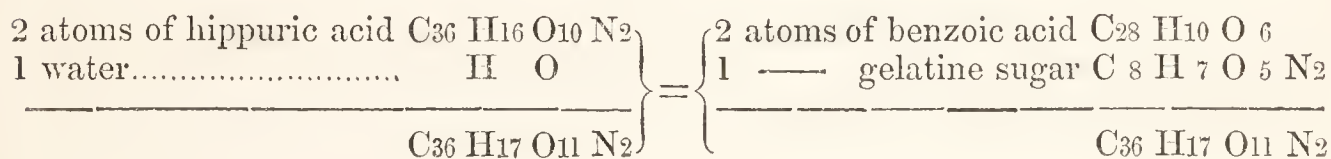
*Bromide of Benzole*,  $C_{12}H_6Br_6$ , is a white insoluble powder, resulting from the action of bromine on benzole. When acted on by an alcoholic solution of potassa, a white crystalline body separates  $= C_{12}H_3Br_3$ ; hence the first bromide may be represented as  $C_{12}H_3Br_3 + 3HBr$ .

*Stilbene. Picramyle.*  $C_{14}H_6$ , or  $C_{28}H_{12}$ . This hydrocarbon was obtained by Laurent, in an isolated state, by fusing the hydruret of sulphobenzoyl in a retort, and continuing the heat till sulphuret of carbon and sulphuretted hydrogen are no longer evolved; the temperature is then increased, when two distinct products are obtained; the first is *stilbene*; it crystallizes in pearly scales; it is succeeded by and mixed with another substance, in acicular crystals, which Laurent calls *sulphessal* (*thionessal*). The stilbene is separated by dissolving the first formed crystals in boiling alcohol, which, on cooling, deposits it in

tabular crystals, leaving the sulphur compound undissolved; and it may be purified by solution in hot ether, which deposits it in crystals having a peculiar pearly lustre resembling the variety of zeolite termed *stilbite* (from  $\sigma\tau\iota\lambda\beta\omega$ , to shine).

Stilbene is fusible and volatile, and more soluble in ether than in alcohol. Its *binoxide* is *bitter almond oil*;  $= \text{C}_{14} \text{H}_6 \text{O}_2$ . It unites with chlorine, bromine, and sulphur. Boiling nitric acid decomposes it and gives rise to several new products.

**HIPPURIC ACID.**  $\text{C}_{18} \text{H}_8 \text{O}_5 \text{N} + \text{HO} = \overline{\text{Hip}} + \text{HO}$ . *Urobenzoic Acid*. This acid was first detected in the urine of the horse and cow by Fourcroy and Vauquelin, and by them regarded as benzoic acid; it was afterwards shewn by Liebig to contain nitrogen, and to exist in human urine. It abounds in the urine of herbivorous mammals, more especially when fed on fresh herbage. Various hypothetical views have been suggested by Pelouze, Mitscherlich, Fehling, and others, respecting its constitution; and Dessaignes has shewn, (*Comptes rendus*, Dec. 1845,) that by the action of acids and alkalis it may be resolved into *benzoic acid* and *gelatine sugar*, or that 2 atoms of hippuric acid include the elements of 2 of benzoic acid, 1 of gelatine sugar, and 1 of water.



Ure and Garrod have shown that when benzoic acid is taken into the stomach it is converted into hippuric acid, which passes off as hippurate of ammonia with the urine. (*Mem. Chem. Soc.*, i. 79.)

Liebig obtained hippuric acid by evaporating the urine of the horse to about one-tenth its bulk, and adding hydrochloric acid, which, after some time produces a brown crystalline deposit; this is boiled with milk of lime and filtered, chloride of lime being added to the hot filtrate, till the urinous odor is destroyed: the liquor is then boiled with animal charcoal, filtered, and hydrochloric acid added; as it cools, crystals of hippuric acid are formed. Fownes has justly observed that very little hippuric acid can be obtained by the preceding process from the horse-urine as usually collected in stables, but that it may be more abundantly procured from cow's urine, as follows (*Mem. Chem. Soc.*, April, 1842): perfectly fresh cow-urine is evaporated in a water-bath to about one-tenth, and mixed with hydrochloric acid; a large quantity of brown hippuric acid separates, which is to be dissolved in boiling water, and a stream of chlorine transmitted through the solution, till the odor of that gas predominates, and the hot liquor loses its brown and acquires a yellow color; it is then filtered, and on cooling, the acid crystallizes, still however very impure. It is therefore dissolved in a hot solution of carbonate of soda, taking care to have a little excess of alkali, digested for a few minutes with animal charcoal, filtered, and strongly acidified by hydrochloric acid, which removes the base and sets the hippuric acid free: should it, however, not be perfectly white, it may be again dissolved in hot water, a little chlorine passed through it, supersaturated by carbonate of soda, and precipitated, as before, by hydrochloric acid. If the urine, instead of



being fresh, is ammoniacal, a slow effervescence, attended by the evolution of ammonia, ensues during its evaporation, and, as Liebig has shown, benzoic acid, with a trace only of hippuric acid, is obtained. The great density of cow's urine is chiefly due to a large quantity of urea, which may be extracted from the brown liquid, after the separation of the hippuric acid, by the aid of a strong hot solution of oxalic acid, which throws down oxalate of urea; this may be decomposed by chalk and the urea obtained without the help of alcohol. (See also GREGORY on the preparation of Hippuric Acid. Mem. Chem. Soc., iii. 330.)

Hippuric acid, when quite pure, crystallizes in four-sided prisms with dihedral summits, semitransparent, slightly bitter, and reddening litmus; if not perfectly pure, it usually forms short radiated needles, or a granular crystalline powder. It fuses when heated, and concretes on cooling into a crystalline mass: it requires about 400 parts of water at 60° for solution; it is abundantly soluble in boiling water and in alcohol, and but little soluble in ether. The *anhydrous acid* consists of

|                               |    |      |     |      |        |
|-------------------------------|----|------|-----|------|--------|
| Carbon .....                  | 18 | .... | 108 | .... | 63·53  |
| Hydrogen .....                | 8  | .... | 8   | .... | 4·70   |
| Oxygen .....                  | 5  | .... | 40  | .... | 23·54  |
| Nitrogen.....                 | 1  | .... | 14  | .... | 8·23   |
| <hr/>                         |    |      |     |      |        |
| Anhydrous hippuric acid ..... | 1  |      | 170 |      | 100·00 |

The *hydrated acid* contains

|                                     |    |      |     |      |        |      |        |      |       |
|-------------------------------------|----|------|-----|------|--------|------|--------|------|-------|
|                                     |    |      |     |      |        |      |        |      |       |
| Dumas and                           |    |      |     |      |        |      |        |      |       |
| Liebig. Peligot. Mitscherlich.      |    |      |     |      |        |      |        |      |       |
| Carbon .....                        | 18 | .... | 108 | .... | 60·34  | .... | 60·96  | .... | 60·5  |
| Hydrogen ....                       | 9  | .... | 9   | .... | 5·03   | .... | 5·09   | .... | 4·9   |
| Oxygen .....                        | 6  | .... | 48  | .... | 26·81  | .... | 26·53  | .... | 26·9  |
| Nitrogen.....                       | 1  | .... | 14  | .... | 7·82   | .... | 7·42   | .... | 7·7   |
| <hr/>                               |    |      |     |      |        |      |        |      |       |
| Crystallised }<br>hippuric acid }   | 1  |      | 179 |      | 100·00 |      | 100·00 |      | 100·0 |
|                                     |    |      |     |      |        |      |        |      |       |
| = {                                 |    |      |     |      |        |      |        |      |       |
| Anhydrous }<br>hippuric }<br>acid } |    |      |     |      |        |      |        |      |       |
| Water.....                          |    |      |     |      |        |      |        |      |       |
| <hr/>                               |    |      |     |      |        |      |        |      |       |
| 1 179 100·00 100·00 100·0 100·00    |    |      |     |      |        |      |        |      |       |
| 1 179 100·00                        |    |      |     |      |        |      |        |      |       |

When hippuric acid is subjected to destructive distillation, benzoic acid, benzoate of ammonia, and a peculiar oily product, which concretes on cooling, are the results; at a higher temperature hydrocyanic acid is formed, and a bulky coal remains. When gradually heated with excess of lime, ammonia, benzine, and carbonate of lime are the results, without the production of cyanogen, or a residue of charcoal. When hippuric acid is boiled with dilute nitric or hydrochloric acid, the liquor deposits benzoic acid on cooling, and gelatine-sugar remains in solution. The same change takes place when the acid is boiled for half an hour with excess of a solution of potassa. In these cases 100 parts of hippuric acid yield between 67 and 68 of benzoic acid. (DESSAIGNE.) When peroxide of lead is boiled with a solution of hippuric acid, the mixture concretes into a crystalline mass of benzamide. (FEHLING.)

*Hippurates.* Those of the alkalis and earths are soluble and crystallizable: with the oxides of the common metals (iron excepted), the compounds are difficultly soluble, but they generally crystallize from their boiling solutions. The hippurate of iron resembles the benzoate. These salts have been principally examined by Schwartz. (*Ann. der Pharm.*, liv. 29. *Chem. Gaz.*, Aug. 1845.)

*Hippurate of Ammonia.* When a solution of the neutral salt is evaporated, it loses ammonia, and passes into an acid salt,  $=\text{NH}_4\text{O}, \text{HO}; 2\text{Hip}; +2\text{HO}$ ; it crystallizes in square prisms, very soluble in water and in alcohol, but difficultly soluble in ether. Heated to between  $360^\circ$  and  $390^\circ$  it loses ammonia, and hippuric acid of a rose-red color remains. *Hippurate of Potassa*,  $\text{KO}, \overline{\text{Hip}} + 2\text{HO}$ , forms a crystalline crust containing rhombic prisms; it loses its water of crystallization when dried at  $212^\circ$ . The acid salt,  $\text{KO}, \text{HO}, 2\overline{\text{Hip}} + 2\text{HO}$ , forms silky lamellar crystals. *Hippurate of Soda* is difficultly crystallizable, and generally of a yellow color, as is also the potassa salt. *Hippurate of Baryta*,  $\text{BaO}, \overline{\text{Hip}} + \text{HO}$ , yields microscopic crystals, deposited on evaporating its solution, which are rendered anhydrous at  $212^\circ$ . *Hippurate of Strontia*,  $\text{SrO}, \overline{\text{Hip}}, + 5\text{HO}$ , crystallizes from its hot solution in a lamellar form; it is difficultly soluble in cold water, and in alcohol, but readily soluble in them when aided by heat. The crystals lose their 5 atoms of water, when dried at  $212^\circ$ . *Hippurate of Lime*,  $\text{CaO}, \overline{\text{Hip}} + 3\text{HO}$ , forms rhombic prisms. *Hippurate of Magnesia*,  $\text{MgO}, \overline{\text{Hip}} + 5\text{HO}$ , crystallizes in mamillary groups; when dried in vacuo, it retains 5 atoms, and at  $212^\circ$ , 1 atom of water of crystallization. *Hippurate of Peroxide of Iron* is thrown down on mixing cold solutions of hippurate of potassa and perchloride of iron, in the form of a brownish voluminous precipitate, insoluble in cold and hot water, but fusing in the latter into a resin-like mass; the dried precipitate is soluble in hot alcohol, and deposited, partly in bundles of red crystals, on cooling. The *hippurates of Cobalt and of Nickel* both crystallize with 5 atoms of water, which are expelled at  $212^\circ$ , leaving blue and green anhydrous salts. *Hippurate of Copper*,  $\text{CuO}, \overline{\text{Hip}} + 3\text{HO}$ , is deposited in prismatic crystals on evaporating a mixed solution of sulphate of copper and hippurate of soda; the salt may be purified by solution in and crystallization from alcohol; it is difficultly soluble, and rendered anhydrous by drying at  $212^\circ$ . *Hippurate of Lead* falls in the form of a caseous precipitate, on adding hippurate of potassa to a solution of acetate of lead; it is soluble in boiling water, and deposited on cooling, in fine silky acicular crystals, containing 2 atoms of water of crystallization, but these rapidly change into four-sided tables with 3 atoms of water; both salts become anhydrous at  $212^\circ$ . *Hippurate of Silver*,  $\text{AgO}, \overline{\text{Hip}}, + \text{HO}$ , is thrown down by double decomposition, insoluble in cold, but soluble in boiling water; it forms microscopic acicular crystals, which at  $212^\circ$  lose 1 atom of water, and the anhydrous salt remains.

AMYGDALINE.  $\text{C}_{40}\text{H}_{27}\text{O}_{22}\text{N}$ . It has been above stated, that neither hydrocyanic acid nor hydruret of benzoyle (bitter almond oil,) are ready formed in the bitter almond, but that those compounds are produced by the mutual agencies of certain azotised substances existing in the kernel, under the influence of water and a due temperature; these substances are *amygdaline*, and *emulsine* (*synaptase*); the latter has already been noticed (p. 1234); the former, together with the phenomena of its transmutations, remains to be described.

Amygdaline was discovered by Robiquet and Boutron-Charlard; (*Ann. Ch. et Ph.*, xLiv. 352); it is found in bitter almonds, in the leaves



and berries of the cherry-laurel, and probably in the kernels of all the bitter species of *amygdalus* and *prunus*, as the peach, plum, apricot, &c. It is obtained as follows: the cake of bitter almonds which remains after the expression of the fixed oil, is boiled in repeated portions of alcohol, of 93 to 94 *per cent.* (sp. gr. 0·812, to 0·815 at 60°,) by which the *synaptase* is rendered inert, and the *amygdaline*, together with some other substances, is abstracted: these alcoholic liquors are then distilled in a water-bath, till the residue acquires a syrupy consistence, when it contains little else than amygdaline and sugar; to get rid of the latter, the liquor is diluted with water, and a little yeast having been added, it is placed in a warm situation so as to ferment; when the fermentation has ceased, the liquor is filtered, and again evaporated in a water-bath to the consistence of syrup; excess of cold alcohol is then added to it, which throws down the amygdaline in the form of a white crystalline powder; it may be dried by pressure between folds of bibulous paper, and redissolved in boiling alcohol, from which it separates on cooling in small silky lamellar or acicular crystals. From 3 to 4 *per cent.* of amygdaline is thus obtained from common bitter almonds. Amygdaline is readily soluble in water; it is very sparingly soluble in cold alcohol, but much more soluble in boiling alcohol, and the crystals deposited from this solution retain alcohol, which however they lose by exposure to air. The crystals deposited from its saturated aqueous solution are transparent prisms, containing 10·57 *per cent.* of water (= 6 atoms); dried *in vacuo* over oil of vitriol they lose 2 atoms of water, = 3·52 *per cent.* Amygdaline is inodorous, but has a slight flavor of bitter almonds; when heated it exhales the odor of may-blossom, and leaves a bulky coal; its components are

|                  |    |     |     |     |        | Liebig. |
|------------------|----|-----|-----|-----|--------|---------|
| Carbon .....     | 40 | ... | 240 | ... | 52·52  | 52·98   |
| Hydrogen .....   | 27 | ... | 27  | ... | 5·90   | 5·84    |
| Oxygen .....     | 22 | ... | 176 | ... | 38·51  | 38·12   |
| Nitrogen.....    | 1  | ... | 14  | ... | 3·07   | 3·06    |
| <hr/>            |    |     |     |     |        |         |
| Amygdaline ..... | 10 |     | 457 |     | 100·00 | 100·00  |

When amygdaline is distilled with dilute nitric acid or other oxidizing agents, ammonia, hydruret of benzoyle, benzoic acid, formic acid, and carbonic acid, are the products. The caustic fixed alkalis convert it into ammonia and amygdalic acid. By the action of permanganate of potassa it is resolved into cyanate and benzoate of potassa.

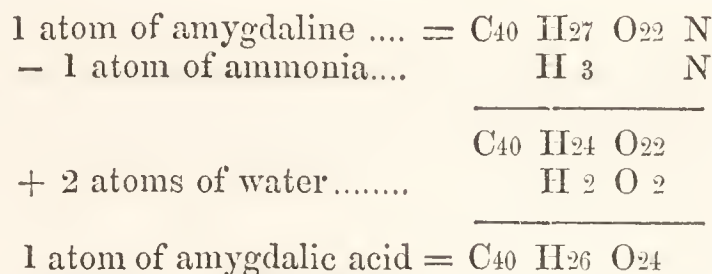
*Amygdalic Acid*,  $C_{40}H_{26}O_{24} + HO$ , was discovered by Liebig and Wöhler. (*Ann. Ch. et Ph.*, LXIV. 195.) It is prepared by boiling amygdaline with baryta as long as ammonia is given off, and then removing the baryta from the soluble amygdalate by means of sulphuric acid. By evaporation in a water-bath, the filtered liquor yields the amygdalic acid, in the form of a colorless, transparent, amorphous, and deliquescent substance of a pleasant acid flavor; it is neither soluble in alcohol nor in ether. It is converted by the action of nitric acid, or of sulphuric acid and peroxide of manganese, into hydruret of benzoyle, formic acid, and carbonic acid.

The *Amygdalates* have been little studied; they are all soluble, with the exception of the basic salt of lead. In the dry *amygdalate of baryta*

the water of the hydrated acid is replaced by baryta, its formula being  $\text{BaO}$ ,  $\text{C}_{40}\text{H}_{26}\text{O}_{24}$ . The elementary composition of the *anhydrous amygdalic acid* is

|                          |    |      |     |      |       | Wöhler and Liebig. |         |
|--------------------------|----|------|-----|------|-------|--------------------|---------|
| Carbon .....             | 40 | .... | 240 | .... | 52.4  | ....               | 52.879  |
| Hydrogen .....           | 26 | .... | 26  | .... | 5.7   | ....               | 5.613   |
| Oxygen .....             | 24 | .... | 192 | .... | 41.9  | ....               | 41.508  |
| <hr/>                    |    |      |     |      |       | <hr/>              |         |
| Anhydrous amygdalic acid | 1  |      | 458 |      | 100.0 |                    | 100.000 |

This acid is formed from amygdaline, by the abstraction of 1 atom of ammonia and the addition of 2 atoms of water :



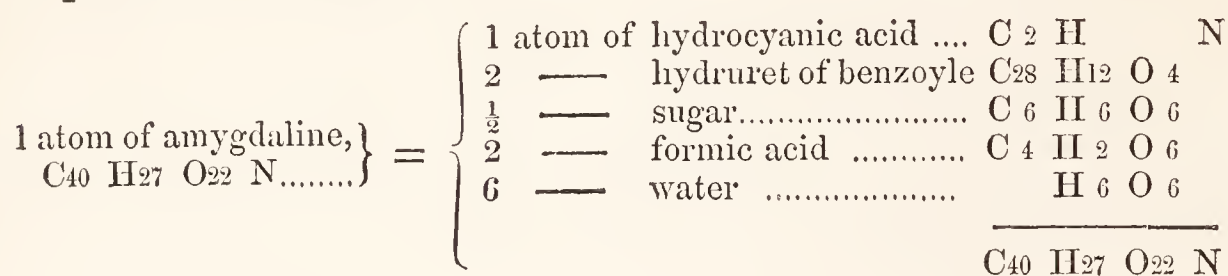
The action of emulsine (synaptase) upon amygdaline, connected with the formation of the crude bitter almond oil, was first explained by Wöhler and Liebig. When a solution of 10 parts of amygdaline in 100 of water is mixed with a solution of 1 part of emulsine in 10 of water, a change immediately ensues; the mixture becomes opalescent, acquires the odor of bitter almonds, and, when distilled, yields hydruret of benzoyle and hydrocyanic acid; these changes ensue most rapidly at a temperature between  $85^{\circ}$  and  $105^{\circ}$ . Boiling water and boiling alcohol entirely suspend and destroy the action. Whether the presence of air is or is not requisite, has not been determined.

When expressed bitter almonds are moistened and triturated with water, the same reaction ensues, and if enough water be present to dissolve the oil as it is formed, the whole of their amygdaline disappears: to obtain the full proportion of oil, 1 part of bitter almond cake should be macerated for 24 hours in 20 parts of water, at about  $100^{\circ}$ , and then subjected to distillation. 100 parts of amygdaline produce, according to Liebig, 47 parts of the crude oil, containing 5.9 parts of hydrocyanic acid; so that 17 grains of amygdaline dissolved in an ounce of emulsion of sweet almonds, yields a solution containing 1 grain of anhydrous hydrocyanic acid. "This mixture has the advantage of containing the hydruret of benzoyle present in the distilled water, to which is perhaps owing the superiority of the distilled oil of bitter almonds, or of laurel leaves, over the more diluted hydrocyanic acid; a superiority which, according to the continental physicians, is very decided and obvious. The above simple recipe given by Liebig and Wöhler, is admirably adapted for extemporaneous use, but the mixture never ought to be made in large quantity at a time, as, like the distilled water, it alters by keeping." (GREGORY. See also WÖHLER and LIEBIG, *Ann. Ch. et Ph.*, XLiv. 209.)

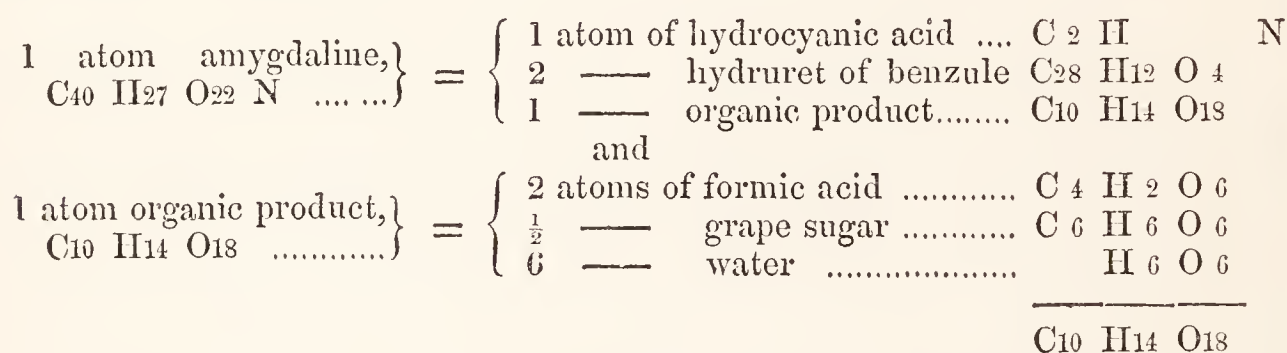
In the remarkable changes which ensue during the mutual action of emulsine and amygdaline under the conditions above stated, bitter almond oil and hydrocyanic acid are not the only products; sugar and formic acid are also formed, and it is not improbable, as Löwig has suggested,



that the amygdaline resolves itself in the first instance into sugar and an azotised compound, which latter, under the further influence of the ferment, yields hydruret of benzoyle, hydrocyanic acid, and formic acid. The general result of this fermentative decomposition of amygdaline may be represented as follows :



It may also be assumed that the amygdaline is in the first instance resolved into hydrocyanic acid, hydruret of benzoyle, and a non-azotised combination, which latter, in the second stage of the process, yields sugar, formic acid, and water.



It will be observed in regard to such of the preceding statements as have reference to the existence of the compound radical *benzoyle*, that it enables us to assimilate a variety of its combinations, with those derived from the elementary radicals. But the composition of benzoyle has led to other views of this series of compounds. Dumas, for instance, represents hydruret of benzoyle as a benzoate of a hydrocarbon = C<sub>14</sub> H<sub>8</sub>; but this hypothesis is needlessly complex, and is inapplicable in many cases which the benzoyle theory readily explains. Mitscherlich considers common benzoic acid as a *bicarbonate of benzoyle*; and a dry benzoate, as containing *benzide* = C<sub>12</sub> H<sub>5</sub>, and *anhydrous oxalic acid* = C<sub>2</sub> O<sub>3</sub>. (See LIEBIG, *Chim. Org.*, i. 279.) But neither of these hypotheses are in any respect preferable to the simpler views above adopted.

XXIV. SALICYLOUS ACID. SALICYLE. SPIROYLE. There is a peculiar oil obtained by distilling the flowers of *Meadowsweet* (*Spiræa ulmaria*) with water, and which was first examined by Pagenstecher (*Ann. Ch. et Ph.*, lxxix. 331,) who found it to consist of an indifferent oil, or hydrocarbon, and a peculiar compound, having acid characters, which was separable from the crude essence by neutralizing it with potassa, and afterwards decomposing the compound by distillation with dilute sulphuric acid. This product has been termed *salicylous acid* or *hydruret of salicyle*, it being identical with a product obtained by Piria, by distilling *salicine*, a crystalline substance derived from *willow bark*, with bichromate of potassa, sulphuric acid, and water.

There is a remarkable analogy between the hydruret of salicyle and the hydruret of benzoyle, and as far as their *basic hydrocarbons* are

concerned, they are identical; but the oxide of hydrocarbon forming the basis of the *salicyle series of compounds*, is  $C_{14}H_5O_4$ , while that of the *benzoyle series* is  $C_{14}H_5O_2$ ; and as bitter almond oil, represented as the *hydruret of benzoyle*, is  $C_{14}H_5O_2 + H$ , so meadowsweet oil, represented as the *hydruret of salicyle*, is  $C_{14}H_5O_4 + H$ .

The principal compounds which, together with their respective combinations, are now to be described, are as follows:

|                       |                      |
|-----------------------|----------------------|
| Salicine .....        | $C_{16}H_{18}O_{24}$ |
| Saligenine .....      | $C_{14}H_8O_4$       |
| Saliretine .....      | $C_{14}H_6O_2$       |
| Salicylous acid ..... | $C_{14}H_5O_3 + HO$  |
| Salicylic acid .....  | $C_{14}H_5O_5 + HIO$ |

SALICINE was discovered in 1830 by Leroux (*Ann. Ch. et Ph.*, xliii. 440,) in the bark of the *Salix Helix*; shortly afterwards, Braconnot detected it in the bark of the *Salix amygdalina* and *Populus tremula*; but there are several varieties of *Salix* and of *Populus* in which no traces of it are to be found. (*Ann. Ch. et Ph.*, xliv. 296.)

Salicine is obtained by boiling willow bark in two or three successive portions of water, and evaporating the decoctions till the concentrated liquor is about thrice the weight of the bark employed; the liquor is then digested for 24 hours with finely pulverised oxide of lead, and the clear liquor evaporated to the consistence of syrup: after some days it forms a crystalline mass, which is separated from the mother liquor, and purified by solution and crystallization. Any remaining lead may be separated by sulphuretted hydrogen, and the solution subsequently decolorized by animal charcoal, and evaporated; it then yields pure salicine.

Salicine may be similarly obtained from the poplar bark, to a decoction of which a slight excess of acetate of lead is added, filtered, and excess of lead removed by dilute sulphuric acid. The liquor is then boiled with the charcoal and filtered whilst hot; on cooling, salicine is deposited, which becomes pure and white after a second solution and crystallization.

Salicine crystallizes in small silky needles of an intensely bitter flavor, soluble in about 20 parts of water at  $60^\circ$ , and very soluble in boiling water. According to Dumas, 100 parts of water dissolve 5.6 of salicine at  $85^\circ$ . Its solubility in alcohol appears to be about the same as in water, but it is insoluble in ether and in volatile oils. It fuses at about  $212^\circ$ , like a fatty body, and on cooling, concretes into a crystalline mass. It consists of

| it consists of |       |     |       |           | Piria.   | Mulder.   | Otto.     | Marchand. |
|----------------|-------|-----|-------|-----------|----------|-----------|-----------|-----------|
| Carbon .....   | 26    | ... | 156   | ... 54.54 | ... 54.8 | ... 54.63 | ... 54.50 | ... 54.44 |
| Hydrogen....   | 18    | ... | 18    | ... 6.29  | ... 6.3  | ... 6.30  | ... 6.28  | ... 6.29  |
| Oxygen.....    | 14    | ... | 112   | ... 39.17 | ... 38.9 | ... 39.07 | ... 39.22 | ... 39.27 |
| <hr/>          | <hr/> |     | <hr/> | <hr/>     | <hr/>    | <hr/>     | <hr/>     | <hr/>     |
| Salicine.....  | 1     |     | 286   | 100.00    | 100.0    | 100.00    | 100.00    | 100.00    |

The changes effected upon salicine by heat and chemical agents are best explained according to Piria (*Ann. Ch. et Ph.*, lix. 281, and 3ème Ser., xiv. 274), by regarding it as a combination of *sugar* and *saligenine*.

|                            |                      |
|----------------------------|----------------------|
| 1 atom of sugar .....      | $C_{12}H_{10}O_{10}$ |
| 1 atom of saligenine ..... | $C_{14}H_8O_4$       |
| <hr/>                      | <hr/>                |
| = 1 atom of salicine ..... | $C_{26}H_{18}O_{14}$ |



SALIGENINE,  $C_{14}H_8O_4$ , is obtained by adding 3 parts of emulsine (synaptase) to 50 parts of finely pulverized salicine diffused in 200 parts of water, and keeping the mixture for 10 or 12 hours upon a sand-bath heated to  $104^\circ$ . The salicine is thus resolved into sugar and saligenine, which latter crystallizes in small aggregated rhomboids. The remaining saligenine may be obtained from the saccharine solution by agitating it with ether, which takes up the saligenine and leaves it on evaporation; it may be purified by repeated crystallization.

Saligenine forms iridescent rhombic crystals when deposited from its hot saturated solution, very soluble in hot water, but requiring 15 parts of water at  $70^\circ$  for solution; it is very soluble in alcohol and in ether; it fuses into a clear liquid, which congeals at  $176^\circ$ . Heated in a retort, to  $212^\circ$ , a small portion of it sublimes in thin brilliant flakes. It consists of

|                  |    |     |     |     |        | Piria. |
|------------------|----|-----|-----|-----|--------|--------|
| Carbon .....     | 14 | ... | 84  | ... | 67.74  | 67.57  |
| Hydrogen.....    | 8  | ... | 8   | ... | 6.45   | 6.54   |
| Oxygen .....     | 4  | ... | 32  | ... | 25.81  | 25.89  |
| Saligenine ..... | 1  |     | 124 |     | 100.00 | 100.00 |

When saligenine is heated to a little above  $212^\circ$ , water, and a trace of salicylic acid, are evolved; when its temperature has been raised to  $285^\circ$  or  $300^\circ$ , it concretes slowly on cooling, and after having been subjected to a higher temperature, it no longer crystallizes, on cooling, but gradually passes, by the loss of 2 atoms of water, into an amber-like substance which is *saliretine*, and which consists of  $C_{14}H_6O_2$ , being *isomeric* with hydruret of benzoyl. [ $C_{14}H_8O_4 = C_{14}H_6O_2 + 2HO$ .]

By the action of certain oxidizing agents, as for instance, chromic acid, bichromate of potassa, or oxide of silver, saligenine may be converted into salicylous (spiroilous) acid [ $C_{14}H_6O_4$ ] and water. [ $C_{14}H_8O_4 + O_2 = C_{14}H_6O_4 + 2HO$ ]. Heated with diluted sulphuric acid and peroxide of manganese, saligenine is resolved into carbonic acid and formic acid; it is decomposed by concentrated nitric acid; but with dilute nitric acid, it forms a deep red solution, and is converted into a resinous substance, which is thrown down on diluting the liquor with water, and the odor of salicylous acid becomes at the same time perceptible.

By dilute hydrochloric, or sulphuric acid, saligenine is resolved into saliretine and water. Concentrated sulphuric acid converts it into *rutiline*, a substance isomeric, according to Mulder, with saliretine, its formula being apparently  $C_{28}H_{12}O_4$ .

Ammonia dissolves saligenine, and under the influence of air, the solution becomes green; it is reddened by acids, and alkalis restore the green color. Boiled in a solution of potassa, saligenine is converted into a resin, which may be precipitated by acids. Fused with caustic potassa hydrogen is evolved, and salicylite (spiroylite) of potassa formed  $= KO$ ,  $C_{14}H_5O_3$ .

*Chlorosaligenine.* When salicine is subjected to the action of chlorine, several products are formed, which may be regarded as combinations of saligenine, in which 1, 2, and 3 atoms of hydrogen have been replaced by a corresponding number of atoms of chlorine, with sugar; digested

with synaptase, the sugar is destroyed and we obtain the following products; (PIRIA.)

|                           |                 |                                  |                |
|---------------------------|-----------------|----------------------------------|----------------|
| Chlorosaligenine .....    | C <sub>14</sub> | $\frac{\text{H}_7}{\text{Cl}}$   | O <sub>4</sub> |
| Bichlorosaligenine .....  | C <sub>14</sub> | $\frac{\text{H}_6}{\text{Cl}_2}$ | O <sub>4</sub> |
| Perchlorosaligenine ..... | C <sub>14</sub> | $\frac{\text{H}_5}{\text{Cl}_3}$ | O <sub>4</sub> |

Of these compounds the first only has been examined and analysed. It crystallises from its hot aqueous solution in rhombic tables exactly resembling saligenine. It dissolves in water, alcohol, and ether; gives a blue tint to the persalts of iron; and is converted by the acids into a *resinoid*, which probably bears the same relation to chlorosaligenine, as saliretine does to saligenine. (LÖWIG.)

The original compounds derived from the action of chlorine upon salicine (before the abstraction of the sugar) have been termed by Piria, *Chlorosalicine*, *Bichlorosalicine*, and *Perchlorosalicine*.

*Chlorosalicine*.  $\text{C}_{26} \text{H}_{17} \text{O}_{14} \text{Cl} + 4\text{HO} = \text{C}_{12} \text{H}_{10} \text{O}_{10} + \text{C}_{14} \text{H}_7 \text{O}_4 \text{Cl} + 4\text{HO}$ . This compound is obtained by passing chlorine through a mixture of 1 part of salicine and 4 of water; it yields at first a yellow solution, and hydrochloric acid is formed; but after a time pearly crystals of chlorosalicine are abundantly deposited; these are agitated with a little ether, and dissolved in hot water. On evaporation, silky acicular crystals are obtained, which are very soluble in water and in alcohol, but insoluble in ether; they are inodorous, and very bitter: they lose 4 atoms of water by drying at  $212^\circ$ , and are then  $\text{C}_{26} \frac{\text{H}_{17}}{\text{Cl}} \text{O}_{14}$ . This substance fuses when adequately heated, and evolves hydrochloric acid, leaving a bulky coal. It is resolved by the action of synaptase into sugar and chlorosaligenine. Diluted acids convert it into sugar and resinous matter. Concentrated sulphuric acid dissolves it, forming a red liquor.

*Bichlorosalicine*,  $\text{C}_{26} \text{H}_{16} \text{O}_{14} \text{Cl}_2 + 2\text{HO} = \text{C}_{12} \text{H}_{10} \text{O}_{10} + \text{C}_{14} \text{H}_6 \text{O}_4 \text{Cl}_2 + 2\text{HO}$ , is obtained by subjecting the preceding compound to the further action of chlorine; the crude product, when washed with ether, and purified by crystallization from its hot aqueous solution, forms long silky needles, of a slightly bitter taste, insoluble in cold, and only sparingly soluble in boiling water. They become anhydrous when dried at  $212^\circ$ , and are then  $\text{C}_{26} \frac{\text{H}_{16}}{\text{Cl}_2} \text{O}_{14}$ . This compound does not affect the color of the persalts of iron: the caustic alkalis increase its solubility in water, and acids again cause its separation in crystals.

*Perchlorosalicine*,  $\text{C}_{26} \text{H}_{15} \text{O}_{14} \text{Cl}_3 + 2\text{HO} = \text{C}_{12} \text{H}_{10} \text{O}_{10} + \text{C}_{14} \text{H}_5 \text{O}_4 \text{Cl}_3 + 2\text{HO}$ , is formed by passing chlorine through bichlorosalicine diffused in water heated to  $176^\circ$ , some morsels of marble being added to prevent decomposition by free hydrochloric acid; after some time the perchlorosalicine separates in the form of a yellow crystalline powder, which is to be shaken with ether, dissolved in warm weak alcohol, and allowed to crystallize; this alcoholic solution and crystallization being repeated till white acicular crystals are obtained. Perchlorosalicine is soluble in weak alcohol, but insoluble in cold, and only very sparingly



soluble in hot water: it is inodorous, but has a bitter taste, and on account of its difficult solubility, is only slowly decomposed by synaptase: its formula, when anhydrous, is  $C_{26} \frac{H_{15}}{Cl_3} O_{14}$ .

SALIRETINE,  $C_{14} H_6 O_2$ , is formed by boiling salicine in dilute sulphuric acid; it generally has a yellowish color, and retains water, which can only be expelled by careful desiccation at a temperature of  $340^\circ$ . It is insoluble in water, and in ammonia, but soluble in alcohol, ether, and acetic acid, from which solutions water precipitates it. It is thrown down from its solution in fixed alkalis by the acids, when it falls in a gelatinous form. It appears, from Piria's latest experiments, as the above formula shows, that saliretine is isomeric with hydruret of benzoyle.

When salicine is acted upon by concentrated sulphuric acid, care being taken to maintain the temperature below  $160^\circ$ , a reddish-blue compound, first observed by Braconnot, is formed, which consists of sulphuric acid in combination with *Rutiline*,  $= 2[C_{14} H_6 O_2] SO_3$ : when dried it is of a violet tint, insoluble in water, alcohol, and ether, but soluble in sulphuric and nitric acid. It combines with bases.

When salicine is added, by small quantities at a time, to concentrated sulphuric acid, a red solution is formed, and on adding water, the excess of salicine falls, and a red compound remains dissolved, which is *Rufine*,  $C_{14} H_7 O_5$ , in combination with sulphuric acid [*Rufosulphuric acid*  $= C_{28} H_{14} O_{10}, 2SO_3 + HO$ .] Mulder has examined the salts which this acid forms with several of the bases.

If sulphuric acid be poured at once upon 50 or 60 grains of salicine, and the temperature not allowed to rise above  $174^\circ$ , no sulphurous acid is formed, and on washing the product with water, a deep olive-green crystalline substance is obtained, which has been termed *Olivine*,  $= C_{14} H_6 O_4$ ; it is insoluble in water, alcohol, ether, oil of turpentine, and olive oil. Gently heated with concentrated sulphuric acid, it yields a red liquor; it is not acted on by dilute sulphuric acid, nor by cold or hot hydrochloric acid, nor by cold nitric acid: hot nitric acid decomposes it. It is insoluble in potassa and in ammonia. (MULDER.)

SALICYLOUS ACID. *Hydrosalicylic Acid. Spiroylous Acid. Essential oil of Spiræa.*  $C_{14} H_5 O_3, HO$ . This compound is also represented as a *hydruret of salicyle*, by the formula  $C_{14} H_5 O_4 + H$ . It is obtained, as already stated, by distilling the dried flowers of *meadowsweet* with water, till the distillate is no longer rendered yellow by potassa; it is then saturated by potassa, taking care to avoid excess, and distilled to dryness. The residue is then decomposed by distilling it with sulphuric, or better, with phosphoric acid, when a part of the salicylous acid appears in the form of an oil, and part remains dissolved in the water which passes over. To purify it, it is dissolved in ether, and the liquor shaken with solution of potassa; the potassa compound is then decomposed by distillation with phosphoric acid, the product dehydrated by chloride of calcium, and ultimately redistilled.

But this acid may also be obtained from *salicine*, 3 parts of which are to be well mixed and triturated with 3 of bichromate of potassa and 24 of water; this mixture is put into a retort, and 4.5 parts of oil of

vitriol, previously diluted with 12 of water, are added to it: as soon as the evolution of gas has ceased, distillation is proceeded with, and continued as long as drops of oil pass over. The crude product is purified as before. (ETTLING. PIRIA.)

Salicylous acid, when pure, is in the form of a colorless liquid, having a strong odor of the blossom of meadowsweet. It has an acrid flavor, and leaves a white spot upon the tongue. Its vapor bleaches litmus paper; it is difficultly soluble in water, and this solution at first reddens, but afterwards gradually bleaches litmus. It dissolves in all proportions in alcohol and in ether; at a temperature of  $0^{\circ}$  it concretes: it boils at about  $385^{\circ}$ . Its sp. gr. at  $55^{\circ}$  is 1.173; the density of its vapor is 4.27. (PIRIA.) The components of this *hydrated acid* are

|                      |    |      |     |      | Wöhler and |      |        |      |          |      |        |
|----------------------|----|------|-----|------|------------|------|--------|------|----------|------|--------|
|                      |    |      |     |      | Liebig.    |      | Piria. |      | Ettling. |      |        |
| Carbon .....         | 14 | .... | 84  | .... | 68·85      | .... | 68·86  | .... | 69·11    | .... | 68·97  |
| Hydrogen .....       | 6  | .... | 6   | .... | 4·92       | .... | 5·04   | .... | 4·89     | .... | 5·06   |
| Oxygen .....         | 4  | .... | 32  | .... | 26·23      | .... | 26·20  | .... | 26·00    | .... | 25·97  |
| <hr/>                |    |      |     |      |            |      |        |      |          |      |        |
| Salicylous acid .... | 1  |      | 122 |      | 100·00     |      | 100 00 |      | 100·00   |      | 100·00 |

This acid is not altered by the action of air, except in the presence of an alkali, and then it gradually blackens from the production of acetic and melanic acid. Heated with excess of potassa, it passes into *salicylic acid*, and the same change is effected by boiling it with chromic acid. Acted upon by chlorine or bromine, it in the first instance forms *chlorosalicylous* and *bromosalicylous acid*, which are represented by



These afterwards become



thus resembling the chlorobenzoic acids, inasmuch as they are not decomposed by water, or by combination with bases. (LÖWIG.)

When a solution of 1 part of salicylous acid in 4 of alcohol is mixed with aqueous ammonia, yellowish spiculæ form, which again disappear when the liquor is gently heated; afterwards it deposits yellow prisms of *Salicylimide* =  $\text{C}_{42}\text{H}_{18}\text{O}_6\text{N}_2$ , and as these are no longer soluble in the liquid from which they were deposited, it is probable that the first-formed salt was *salicylite of ammonia*, which afterwards, by the action of excess of ammonia, passed into salicylimide.

The salicylous acid, regarded as a *hydracid*, forms compounds which have been termed *salicylurets* or *salicylides*. This acid expels carbonic acid from the alkalis, even in the cold; its salts are either difficultly soluble, or insoluble in water. Both the acid and its salts produce an intensely blue or violet color with the persalts of iron, which, on exposing the solution to the air, gradually disappears. The salts of this acid have been principally examined by Ettling. (*Ann. Ch. et Ph.*, 3ème Ser., i. 493.)

*Salicylite of Potassa.*  $\text{KO, C}_{14}\text{H}_5\text{O}_3 + 2\text{HO}$ . *Salicyluret of Potassium.*  $\text{K, C}_{14}\text{H}_5\text{O}_4$ . This salt is formed by dropping a solution of potassa into an alcoholic solution of salicylous acid, till the mixture concretes; alcohol is then added, and heat applied so as to dissolve the product; on cooling, it is deposited in pearly tabular crystals, which contain



2 atoms of water of crystallization; it becomes anhydrous when dried at  $250^{\circ}$ , and then consists of

|                                  |   |     |     |     | Ettling. |     |        |                                 |   |       |     |     |        |  |
|----------------------------------|---|-----|-----|-----|----------|-----|--------|---------------------------------|---|-------|-----|-----|--------|--|
| Potassa .....                    | 1 | ... | 48  | ... | 29·82    | ... | 28·83  | Potassium ....                  | 1 | ...   | 40  | ... | 24·84  |  |
| Salicylic acid....               | 1 | ... | 113 | ... | 70·18    | ... | 71·17  | Salicyle .....                  | 1 | ...   | 121 | ... | 75·16  |  |
| <hr/>                            |   |     |     |     | <hr/>    |     |        |                                 |   | <hr/> |     |     |        |  |
| Salicylite of }<br>potassa.....} | 1 |     | 161 |     | 100·00   |     | 100·00 | Salicyluret of }<br>potassium } | 1 |       | 161 |     | 100·00 |  |

When the preceding salt is dissolved in hot alcohol, and salicylous acid added till spicular, and not tabular crystals, are deposited on cooling, they constitute an acid salt, and are composed of

|                              |   |     |       |     |        |     | Ettling. |
|------------------------------|---|-----|-------|-----|--------|-----|----------|
| Potassa .....                | 1 | ... | 48    | ... | 16.96  | ... | 17.01    |
| Water .....                  | 1 | ... | 9     | ... | 3.18   | }   | 82.99    |
| Salicylous acid.....         | 2 | ... | 226   | ... | 79.86  |     |          |
| <hr/>                        |   |     | <hr/> |     | <hr/>  |     | <hr/>    |
| Bisalicylite of potassa..... | 1 |     | 283   |     | 100.00 |     | 100.00   |

*Salicylite of Baryta.*  $\text{BaO}, \text{C}_{14} \text{H}_5 \text{O}_3 + 2\text{HO}$ . When this salt is formed by double decomposition from mixed solutions of salicylite of potassa and chloride of barium, it constitutes a crystalline yellow powder; it is very difficultly soluble in cold water, and crystallizes from its hot solution in yellow needles.

*Salicylite of Lead.* When an alcoholic or aqueous solution of salicylous acid is added to basic acetate of lead, a precipitate gradually falls, which re-dissolves on the application of heat, and is deposited in yellow crystalline grains as the liquor cools; it is an anhydrous basic salt =  $2\text{PbO}, \text{C}_{14} \text{H}_5 \text{O}_3$ .

*Salicylite of Copper.*  $\text{CuO}, \text{C}_{14} \text{H}_5 \text{O}_3$ . A dilute alcoholic solution of salicylous acid, added to a cold solution of neutral acetate of copper, produces a crystalline deposit composed of

|                            |   |     |     |     | Ettling. |     |        |  |  |
|----------------------------|---|-----|-----|-----|----------|-----|--------|--|--|
| Oxide of copper .....      | 1 | ... | 40  | ... | 25.68    | ... | 25.55  |  |  |
| Salicylous acid.....       | 1 | ... | 113 | ... | 74.32    | ... | 74.45  |  |  |
| <hr/>                      |   |     |     |     | <hr/>    |     |        |  |  |
| Salicylite of copper ..... | 1 |     | 153 |     | 100.00   |     | 100.00 |  |  |

*Nitrosalicylous Acid.*  $\text{C}_{14} \text{H}_4 \text{O}_3, \text{NO}_4 + \text{HO}$ . When salicylous acid is mixed with dilute nitric acid, and moderately heated, a compound is produced, which may be obtained in yellow crystals from its alcoholic solution. It is sparingly soluble in water, but abundantly in alcohol and in ether; it tinges the cuticle indelibly yellow: its taste is at first slight, but after a time it excites cough and irritation. When carefully heated, it may be sublimed without decomposition. It yields crystalline compounds with the alkaline bases.

**SALICYLIC ACID.** *Spiroylic Acid.*  $\text{C}_{14} \text{H}_5 \text{O}_5 + \text{HO}$ . This acid was discovered by Piria; Cahours has announced its presence, in combination with oxide of methyle, in the oil of the *Gaultheria procumbens*, and there are many cases in which it is artificially produced, some of which are of much theoretical interest. The *anhydrous acid* has not been isolated: its components are

|                              |    |      |     |      |        |
|------------------------------|----|------|-----|------|--------|
| Carbon .....                 | 14 | .... | 84  | .... | 65·12  |
| Hydrogen.....                | 5  | .... | 5   | .... | 3·87   |
| Oxygen.....                  | 5  | .... | 40  | .... | 31·01  |
| <hr/>                        |    |      |     |      |        |
| Anhydrous salicylic acid.... | 1  |      | 129 |      | 100·00 |

The *hydrated acid* consists of

|                                    |    |     |     |        |        | 1      |        | 2         |       | 3          |        | 4        |        | 5        |        |
|------------------------------------|----|-----|-----|--------|--------|--------|--------|-----------|-------|------------|--------|----------|--------|----------|--------|
|                                    |    |     |     |        |        | Piria. |        | Gerhardt. |       | Delalande. |        | Ettling. |        | Cahours. |        |
| Carbon .....                       | 14 | ... | 84  | ...    | 60·86  | ...    | 61·10  | ...       | 60·91 | ...        | 60·8   | ...      | 60·80  | ...      | 60·76  |
| Hydrogen .....                     | 6  | ... | 6   | ...    | 4·35   | ...    | 4·45   | ...       | 4·47  | ...        | 4·5    | ...      | 4·51   | ...      | 4·41   |
| Oxygen .....                       | 6  | ... | 48  | ...    | 34·79  | ...    | 34·45  | ...       | 34·62 | ...        | 34·7   | ...      | 34·69  | ...      | 34·83  |
| <hr/>                              |    |     |     |        |        |        |        |           |       |            |        |          |        |          |        |
| Hydrated sali-<br>cyclic acid .... | }  | 1   | 138 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00    | 100·0 | 100·00     | 100·00 | 100·00   | 100·00 | 100·00   | 100·00 |
|                                    |    |     |     |        |        |        |        |           |       |            |        |          |        |          |        |

(1 was from salicylous acid; 2 from salicine; 3 from coumarine; 4 from benzoate of copper; 5 from oil of gaultheria.)

Salicylic acid (hydrated) may be obtained—(1,) by heating salicylous acid with excess of caustic potassa; it first becomes brown, and then evolves hydrogen and loses color; when gas is no longer evolved, the product is removed from the fire, and dissolved in water, to which hydrochloric acid is added. The salicylic acid separates in crystalline films, and may be obtained from its hot solution in pure colorless crystals. By the same process it may be prepared from saligenine. (2.) Salicine is added in small successive portions to about thrice its weight of hydrate of potassa fused in a silver basin; the mixture becomes brown and evolves hydrogen: when this ceases, and the brown mass has lost its color, it is dissolved in water, and supersaturated with hydrochloric acid. Salicylic acid gradually crystallizes, and may be purified by recrystallization from its hot aqueous solution. (GERHARDT.) (3.) By the same process it may be obtained from Coumarine. (DELALANDE.) (4.) When the oil of *Gaultheria procumbens* is heated with solution of potassa to 112°, methylic alcohol evaporates, and a solution of salicylate of potassa remains, which, decomposed by hydrochloric acid, yields the salicylic acid, as in the preceding cases. (CAHOURS.) (5.) Salicylic acid is formed by the action of fused potassa upon *indigo* at a temperature not exceeding 570°, and may be separated from the fused mass by hydrochloric acid. (CAHOURS.)

This acid separates from its hot aqueous solution in delicate crystals resembling benzoic acid. During the spontaneous evaporation of its alcoholic solution, it forms four-sided prisms; but the most splendid crystals are those obtained by the slow evaporation of its solution in ether from a tall jar closed with paper. When this acid is sublimed, it closely resembles sublimed benzoic acid. It is little soluble in cold water, more so in hot water, and largely soluble in alcohol and in ether. Hot oil of turpentine dissolves about one-fifth of its weight of salicylic acid, and the solution solidifies when cold. The taste of this acid is sweetish, and it irritates the throat; its solution strongly reddens litmus. It fuses at about 300°, and evaporates without decomposition at a higher temperature. When suddenly subjected to a high temperature, it is decomposed with the production of *spirole*, the composition of which is identical with that of *hydrate of phenile* or *carbolic acid*, being C<sub>12</sub> H<sub>6</sub> O<sub>2</sub>. The same product is obtained by heating the acid with baryta or lime; or



by distilling the salicylates of the fixed alkalis: in the former case,  $C_{14}H_6O_6 + 2BaO = C_{12}H_6O_2 + 2[BaO, CO_2]$ . When an alkaline solution of salicylic acid is exposed to air, it gradually assumes a dark blue color.

Salicylic acid is energetically acted upon by strong nitric acid, and a yellow resin-like substance is formed, which when washed with cold, and then dissolved in boiling water, yields crystals of *nitrosalicylic* and *nitropicric* acids. Distilled with dilute sulphuric acid and oxide of manganese, salicylic acid yields formic acid. Chlorine and bromine act upon salicylic as upon the salicylous acid, forming two chloric and three bromic compounds, constituted, according to Cahours, as follows:

|                                |  |
|--------------------------------|--|
| Monochlorosalicylic acid ..... | HO, $C_{14} \begin{smallmatrix} H_4 \\ Cl \end{smallmatrix} O_5$   |
| Bichlorosalicylic acid.....    | HO, $C_{14} \begin{smallmatrix} H_3 \\ Cl_2 \end{smallmatrix} O_5$ |
| Monobromosalicylic acid .....  | HO, $C_{14} \begin{smallmatrix} H_4 \\ Br \end{smallmatrix} O_5$   |
| Bibromosalicylic acid.....     | HO, $C_{14} \begin{smallmatrix} H_3 \\ Br_2 \end{smallmatrix} O_5$ |
| Tribromosalicylic acid .....   | HO, $C_{14} \begin{smallmatrix} H_2 \\ Br_3 \end{smallmatrix} O_5$ |

*Salicylates. Spiroylates.* The general formula of these salts, which have principally been examined by Cahours, is  $MO, C_{14}H_5O_5$ . The *salicylates of ammonia, potassa, soda, lime, baryta, strontia, magnesia*, and *oxide of zinc*, are easily soluble; those of *oxide of copper, lead, and silver*, are difficultly soluble in water. When a solution of pernitrate of iron is dropped upon a crystal of salicylic acid, it renders it as black as ink, and if the acid be dissolved in water, a mere trace of the salt of iron gives it a violet-blue tint. Salicylic acid expels carbonic acid from the carbonates.

*Nitrosalicylic Acid.*  $C_{14}H_4O_5, NO_4, + HO$ . *Nitrospiroylic Acid.* *Indigotic Acid. Anilic Acid.* This compound is formed by digesting a mixture of salicylic acid and moderately strong nitric acid, in a water-bath; on cooling it yields crystals, which require purification by a second solution and crystallization. It may also be obtained by the action of nitric acid on Gaultheria oil. This compound is identical with *indigotic* or *anilic acid*, and is formed by the action of dilute nitric acid upon *indigo* (which see.)

When quite pure, nitrosalicylic acid forms stellated groups of acicular crystals, of a bitter, astringent, and slightly acid taste. When cautiously heated, it may be sublimed without decomposition, and its vapor condenses in the form of white needles. It is soluble in all proportions in boiling water, and very soluble in alcohol, but it requires not less than 1000 parts of water at  $50^\circ$  for its solution. The crystals which form in its aqueous solution contain 4 atoms of water, 3 of which are expelled by drying at between  $300^\circ$  and  $450^\circ$ . The acid then consists of

|                              |    |      |     |      | Marchand.<br>(From salicylic<br>acid.) | Cahours.<br>(From gaul-<br>theria oil.) | Dumas.<br>(From<br>indigo.) |
|------------------------------|----|------|-----|------|--|---|-----------------------------|
| Carbon .....                 | 14 | .... | 84  | .... | 45.90                                  | ....                                    | 45.9                        |
| Hydrogen ....                | 5  | .... | 5   | .... | 2.73                                   | ....                                    | 3.0                         |
| Oxygen .....                 | 10 | .... | 80  | .... | 43.72                                  | ....                                    | 43.3                        |
| Nitrogen .....               | 1  | .... | 14  | .... | 7.65                                   | ....                                    | 7.8                         |
| <hr/>                        |    |      |     |      |  |   |                             |
| Nitrosalicylic<br>acid ..... | 1  |      | 183 |      | 100.00                                 |   | 100.0                       |

The salts of this acid are almost all of a yellow color, and a bitterish taste; when heated they deflagrate like gunpowder. The acid expels carbonic acid from the carbonates, and strikes a deep red color with persalts of iron; it does not affect the protosalts of that metal, nor does it precipitate a solution of gelatine.

PHLORIDZINE. (*φλοιος*, bark, *ρίζα*, root.) This is a crystallizable substance found in the bark of the roots of apple, pear, plum, and cherry-trees, giving it its bitter astringency. It also exists, but in very small quantity, in the leaves, and in the bark of the trunk and branches. It was discovered by Köninck, (*Ann. Ch. et Ph.*, lxi. 151,) and is in many respects very analogous to salicine. It may be best obtained by digesting the bark, recently stripped from the root, for 8 or 10 hours in proof spirit, at a temperature between 120° and 140°; on cooling this infusion, crystals of phloridzine are deposited; they are purified by solution in boiling water, decoloration by animal charcoal, and filtering whilst hot; as the liquor cools, the phloridzine crystallizes in the form of silky needles and tables, of a yellowish white tint.

Phloridzine is very soluble in boiling water, and in alcohol and ether, but it requires about 1000 parts of cold water for solution, so that it is easily obtained in a crystalline mass by cooling its hot aqueous solution; and when its saturated alcoholic solution is diluted it falls in crystals: its specific gravity is 1.43. Its taste is bitter and astringent. At about 228° it enters into perfect fusion, but if the temperature be raised to 266°, it becomes solid, and resembles gum arabic. At about 320° it again fuses, and may be heated, without decomposition, to about 380°. After having been fused at 266°, it dissolves less readily in hot water, and separates from it in the form of an amorphous powder; but when boiled in water, it again crystallizes as usual. If it be heated above 380°, it boils, evolves water, and acquires a red color; and at about 590°, it is decomposed with the usual products of non-azotized organic bodies. (STASS. *Ann. Ch. et Ph.*, lxi. 367.)

Phloridzine has been repeatedly analyzed with similar results, but different formulæ have been suggested for the expression of its composition. Mulder uses the formula  $C_{21}H_{15}O_{12} = C_{21}H_{11}O_8 + 4HO$ , and this is adopted by Marchand. Liebig's formula is  $C_{42}H_{23}O_{18} + 6HO$ . The former,  $C_{21}H_{11}O_8 + 4HO$ , for *crystallized phloridzine*, is upon the whole, most consistent with the analyses of such of the compounds of this substance, as have been accurately examined, and is adopted by Löwig, (*Chem. der Org. verbind.*, i. 914); it gives the following results:



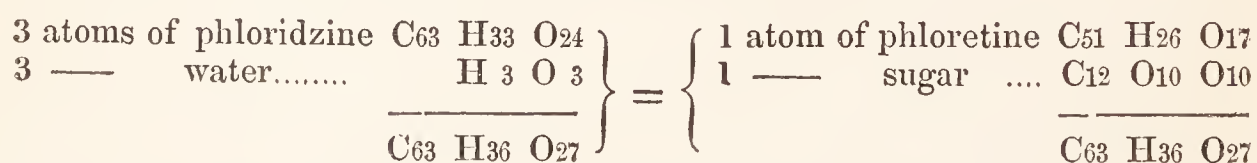
|                              |    |      |     |      |        | Stass. |       | Mulder.    |
|------------------------------|----|------|-----|------|--------|--------|-------|------------|
| Carbon.....                  | 21 | .... | 126 | .... | 53.17  | ....   | 53.8  | .... 53.98 |
| Hydrogen .....               | 15 | .... | 15  | .... | 6.33   | ....   | 6.1   | .... 6.12  |
| Oxygen .....                 | 12 | .... | 96  | .... | 40.50  | ....   | 40.1  | .... 39.90 |
| <hr/>                        |    |      |     |      |        |        |       |            |
| Crystallized phloridzine.... | 1  |      | 237 |      | 100.00 |        | 100.0 | 100.00     |

The formula of the *fused phloridzine* is, upon the same authorities,  $C_{21}H_{11}O_8 + 2HO$ ; and *anhydrous phloridzine*, as combined with bases, consists of

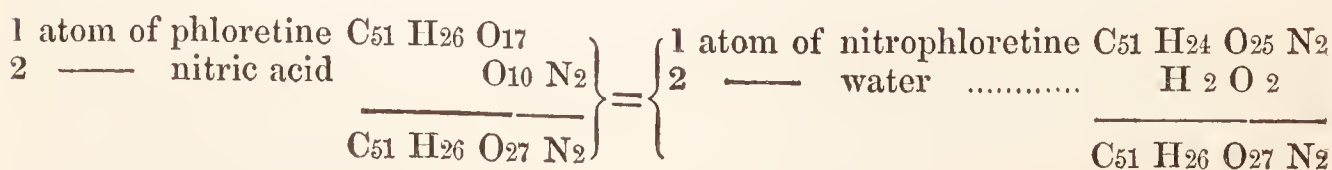
|                             |    |      |     |      |        | Stass.    |
|-----------------------------|----|------|-----|------|--------|-----------|
| Carbon.....                 | 21 | .... | 126 | .... | 62.69  | .... 62.6 |
| Hydrogen .....              | 11 | .... | 11  | .... | 5.47   | .... 5.4  |
| Oxygen .....                | 8  | .... | 64  | .... | 31.84  | .... 32.0 |
| <hr/>                       |    |      |     |      |        |           |
| Anhydrous phloridzine ..... | 1  |      | 201 |      | 100.00 | 100.0     |

Phloridzine readily dissolves in solutions of the alkalis, forming yellow liquors, from which it may be precipitated, unchanged, by the acids. When phloridzine is digested with thin cream of lime, the filtered liquor yields when evaporated *in vacuo*, a compound of 4 atoms of lime with 3 of phloridzine: this combination has the property of copiously dissolving hydrated oxide of copper. When subacetate of lead is dropped into a boiling aqueous solution of phloridzine, so as to leave the latter in excess, a yellowish white precipitate falls, which, after having been dried at  $285^\circ$ , consists, according to Mulder, of  $3PbO + C_{21}H_{11}O_8 + HO$ . When a solution of phloridzine is added to perchloride of iron, the liquor assumes a fine purple tint.

Sulphuric, hydrochloric, phosphoric, and hydriodic acids, dissolve phloridzine without decomposing it, both in their diluted and undiluted states; but when their action is long continued, or aided by heat, the phloridzine is resolved into *sugar* and *Phloretine*.



*Phloretine*,  $C_{51}H_{26}O_{17}$ , is obtained by heating a solution of phloridzine in dilute sulphuric acid, to about  $195^\circ$ ; on cooling, crystalline phloretine separates in small scales of a sweetish taste; it is scarcely soluble even in boiling water, and only sparingly soluble in ether; but alcohol, pyroligneous spirit, and boiling acetic acid, dissolve it abundantly, and deposit it, on cooling, in small shining crystals. Phloretine fuses at  $356^\circ$ , and is decomposed at higher temperatures. Nitric acid converts it into an uncrystallizable brown insoluble substance, *nitrophloretine* (*phloretinic acid*) =  $C_{51}H_{24}O_{25}N_2$ .



*Phloridzène*. This name has been applied to a product of the joint action of oxygen and ammonia on phloridzine; it is best formed by placing several small saucers containing moistened phloridzine, over

a shallow dish containing a solution of sal ammoniac with some pieces of caustic potassa, and covering the whole with a bell-glass. After 24 hours, the layer of moistened phloridzine in each of the saucers should be stirred up, some fresh pieces of potassa added to the solution of sal ammoniac, and the whole covered as before, and these operations should be repeated for three or four times. After 4 or 5 days the phloridzine will be found changed into an almost black liquor; this is to be deprived of free ammonia by exposure *in vacuo* over sulphuric acid, and the residue then diluted with a little water, and mixed with excess of alcohol, so as to dissolve the uncombined phloridzine, and leave a blue substance, which is a combination of phloridzène and ammonia, and which is to be washed with alcohol, then dissolved in water, and decomposed by dropping into it an alcoholic solution of acetic acid, care being taken that the latter is not in excess; the phloridzène is thus precipitated, and requires to be washed a few times with alcohol and then dried.

Phloridzène is an uncrystallizable gum-like substance, of a red color, more soluble in hot than in cold water, and yielding a red aqueous solution; but it scarcely tinges alcohol, pyroligneous spirit, or ether. When the aqueous solution of *phloridzène-ammonia* is acted upon by deoxidizing substances, it instantly loses its color; sulphuretted hydrogen and sulphuret of ammonium decolor it with the separation of sulphur, but the colorless solution, when exposed to air, absorbs oxygen, and again becomes blue. The dilute acids, excepting nitric acid, form red solutions with phloridzène. Chlorine instantly decomposes it. When a solution of phloridzène-ammonia is added to nitrate of silver, a blue precipitate falls.

XXV. CINNAMIC ACID. The essential oil obtained by distilling cinnamon bark with water, and constituting the common *commercial oil of cinnamon*, consists, according to the analysis of Mulder, (*Poggend.*, xli. 398) of  $C_{20}H_{11}O_2$ ; when long exposed to the air it absorbs oxygen, and forms two *resins*, and another oil  $= C_{18}H_8O_2$ . This oil has been represented as the *hydruret* of a supposed radical  $= C_{18}H_7O_2$ , and which has been termed *cinnamyle*. But it is more convenient to apply the term *cinnamyle* to the *hydrocarbon* only, and then we have the following series of compounds.

|                                   |                    |
|-----------------------------------|--------------------|
| Cinnamyle .....                   | $C_{18}H_7$        |
| Oxide of cinnamyle .....          | $C_{18}H_7O$       |
| Hydrated oxide of cinnamyle ..... | $C_{18}H_7O, HO$   |
| Cinnamic acid .....               | $C_{18}H_7O_3$     |
| Hydrated cinnamic acid .....      | $C_{18}H_7O_3, HO$ |

Of these compounds, cinnamyle, oxide of cinnamyle, and anhydrous cinnamic acid, have not been isolated.

*Hydrated Oxide of Cinnamyle*,  $C_{18}H_8O_2 = C_{18}H_7O + HO$ ; or if, as above stated, it be termed a *hydruret*, its rational formula would be  $C_{18}H_7O_2 + H$ . This compound is generally contained in considerable proportion in common oil of cinnamon, and may be procured by distilling old oil of cinnamon which has been exposed to the air; or, more certainly, by the action of hot water upon its *nitrate*; when thus separated, it must be redistilled with water, and dried over chloride of calcium. It is a fragrant oil, colorless, or of a slight yellow tint, and of an



agreeable cinnamon odor; it has a pungent burning flavor. It has been analysed by Mulder, and by Dumas and Peligot (*Ann. Ch. et Ph.*, Lxvii), with the following results:

|                              |    |     |     |     |        | Mulder. | Dumas and<br>Peligot. |     |       |
|------------------------------|----|-----|-----|-----|--------|---------|-----------------------|-----|-------|
| Carbon .....                 | 18 | ... | 108 | ... | 81·81  | ...     | 81·77                 | ... | 81·8  |
| Hydrogen .....               | 8  | ... | 8   | ... | 6·06   | ...     | 6·12                  | ... | 6·1   |
| Oxygen .....                 | 2  | ... | 16  | ... | 12·13  | ...     | 12·11                 | ... | 12·1  |
| <hr/>                        |    |     |     |     |        |         |                       |     |       |
| Purified oil of cinnamon.... | 1  |     | 132 |     | 100·00 |         | 100·00                |     | 100·0 |

*Cinnamic Acid.* C<sub>18</sub> H<sub>7</sub> O<sub>3</sub> + HO. This acid is frequently deposited in crystals, by old oil of cinnamon, and may be purified by dissolving it in boiling water and filtering whilst hot; it forms small brilliant crystals as the liquor cools. Cinnamic acid may also be obtained by adding an alcoholic solution of caustic potassa to a solution of *Peruvian balsam* in alcohol, as long as it occasions a precipitate; on adding water to the alcoholic liquor, a heavy oil separates, which is to be removed, and the remaining solution distilled to obtain the alcohol; from the remaining liquor the cinnamic acid may be precipitated by dilute hydrochloric acid, and washed with a little cold water.

The *heavy oil* obtained in this process has been termed *cinnamène*, or *Peruvine*; it is inodorous, nearly tasteless, insoluble in water, but soluble in alcohol and in ether, and consists, according to Fremy (*Ann. Ch. et Ph.*, Lxx. 180), and Plantamour (*Ann. der Pharm.*, xxvii. and xxx.), of C<sub>54</sub> H<sub>26</sub> O<sub>8</sub>.

Stenhouse obtained cinnamic acid by boiling *liquid storax* for two days with a strong solution of caustic soda, and diluting the alkaline solution, when cold, with a large quantity of water, to precipitate the resin; it was then filtered, and the cinnamic acid precipitated by hydrochloric acid, and purified by repeated crystallization from its hot aqueous solution, or from its solution in alcohol, or by subliming it.

Cinnamic acid forms pearly, lamellar, or prismatic crystals. In many respects it resembles benzoic acid, like which it is very sparingly soluble in cold water, but abundantly soluble in alcohol; it fuses at about 250°, boils at 560°, and may be sublimed without residue. The *anhydrous acid* (as contained in *cinnamate of silver*) has the equivalent 139, (DUMAS and PELIGOT, *Ann. Ch. et Ph.*, Lvii. 305,) being composed of

|                              |    |      |     |      | Dumas and Peligot. |           |
|------------------------------|----|------|-----|------|--------------------|-----------|
| Carbon.....                  | 18 | .... | 108 | .... | 77·69              | .... 78·0 |
| Hydrogen .....               | 7  | .... | 7   | .... | 5·04               | .... 5·4  |
| Oxygen .....                 | 3  | .... | 24  | .... | 17·27              | .... 16·6 |
| <hr/>                        |    |      |     |      |                    |           |
| Anhydrous cinnamic acid .... | 1  |      | 139 |      | 100·00             | 100·00    |

The ultimate elements of the *crystallized acid* are:

|                            |    |     |     |     |        | Dumas and Peligot. |        |
|----------------------------|----|-----|-----|-----|--------|--------------------|--------|
| Carbon.....                | 18 | ... | 108 | ... | 72.97  | ...                | 73.19  |
| Hydrogen .....             | 8  | ... | 8   | ... | 5.41   | ...                | 5.80   |
| Oxygen .....               | 4  | ... | 32  | ... | 21.62  | ...                | 21.01  |
| <hr/>                      |    |     |     |     |        |                    |        |
| Crystallised cinnamic acid | 1  |     | 148 |     | 100.00 |                    | 100.00 |

When a mixture of baryta, or lime, and cinnamic acid, is subjected to

dry distillation, the principal product is *benzine*. (MITSCHERLICH, *Lehrbuch*. BLYTHE and HOFFMANN. *Ann. der Pharm.*, liii. 321.)

By the action of chlorine, or of chloride of lime, cinnamic acid is converted into benzoic acid, and chlorobenzoic acid, and at the same time a peculiar aromatic oil is formed. (STENHOUSE.) By the action of hot nitric acid upon cinnamic acid, it is converted into benzoic and nitrobenzoic acid; but if cold nitric acid be used, and the temperature maintained below  $120^{\circ}$ , *nitrocinnamic acid* is formed. ( $C_{18}H_7O_3 + NO_5 = C_{18}H_6O_3,NO_4 + HO$ . (MITSCHERLICH.) This is a fusible crystalline substance, which at  $70^{\circ}$  requires 327 parts of alcohol for its solution, in which respect it differs from benzoic, and nitrobenzoic acid, and from cinnamic acid. Its salts have been examined by Mitscherlich. By the action of fuming sulphuric acid upon cinnamic acid, Herzog obtained a combination which he has termed *sulphocinnamic acid*; its formula is  $C_{18}H_8O_4,2SO_3$ : it appears to be a *bibasic acid*. (BERZELIUS' *Lehrbuch*, iv. 374. LÖWIG, *Chem. der Org. verb.*, ii. 722.)

By the action of an alcoholic solution of potassa upon *cinnamène*, Plantamour obtained a compound which he has designated *Myroxyllic acid*, (from *Myroxylon Peruvianum*, the *Peruvian balsam tree*,) and of which he has described the principal combinations.

XXVI. SUCCINIC ACID.  $C_4H_2O_3,HO=\overline{Suc} + HO$ . This acid, as its name imports, is generally obtained from *amber* (*succinum*), a substance usually regarded as a fossil resin, and chiefly brought from the southern coast of the Baltic, where it is thrown up upon the beach between Königsberg and Memel; it also occurs in beds of brown coal, and of bituminous wood. It is transparent, or translucent, and of various shades of yellow and brown; its specific gravity fluctuates between 1.06 and 1.07. It is considered by Berzelius as a mixture of two resins, bitumen, volatile oil, and succinic acid. When heated in the air it fuses and burns, exhaling a peculiar and somewhat aromatic odor. It is used for various ornamental purposes, and is the basis of an excellent varnish, but peculiar management is required to effect its solution either in alcohol or in oils. *Oil of amber* is used in medicine; but amber is chiefly interesting to the chemist as yielding *succinic acid*, traces of which are also found in the resins of the *coniferæ*. According to Köncke, the acid of the *Lactuca virosa* and *sativa* (*Lactucic acid*) is identical with succinic acid, and it also occurs, according to Zwenger, in *wormwood*. (*Absynthic acid*).

Succinic acid is obtained from the small pieces of amber which are inapplicable to ornamental purposes, and chiefly used for the manufacture of varnish. These are subjected to distillation in a glass retort, connected by an adapter with a tubulated receiver; or, if the process is conducted upon the large scale, a copper alembic and glass receiver may be employed. The amber first fuses, and yields a watery liquid containing acetic acid, which is followed by empyreumatic oil, and succinic acid, part of which crystallizes in the neck of the retort and in the receiver, and part dissolves in the empyreumatic liquor. During the formation of these products, the matter in the retort swells up considerably, but after a time it suddenly subsides, and the operation should then be stopped, for there is no further production of succinic acid, but a dark-colored thick oil is formed, which soils the other products. This



would be succeeded by a thinner oil, and ultimately a yellow waxy matter would rise, which is yielded by many of the resins under the same circumstances, but which has not been particularly examined. By thus conducting the distillation, 16 ounces of amber yield about half an ounce of rough succinic acid, 3 ounces of oil, and somewhat more than 10 ounces of torrefied resin, fit for the preparation of varnish. When the production of the *acid* is the only object of the operation, Julien recommends coarsely pulverizing the amber, and mixing with it, previous to distillation, a twelfth part of sulphuric acid diluted with its weight of water; about twice as much acid, he says, will thus be obtained, as when the amber is merely heated alone. (*Ann. of Phil.*, ii. 76.) By thus conducting the operation, 2 ounces of crystallized acid may be procured, according to Dumas, from a pound of amber. (*Chim. App. aux Arts*, v. 224.)

The crude acid obtained by these processes is always considerably contaminated by empyreumatic oil; it may be purified, either by the action of chlorine, or by boiling it with nitric acid diluted with about twice its bulk of water, till it crystallizes colorless, and then redissolving the decolored acid in water and recrystallizing: or the impure acid may be saturated with ammonia, and the resulting *succinate of ammonia* purified by crystallization and by filtration through animal charcoal, and then decomposed by acetate of lead; the precipitated *succinate of lead* may then be decomposed by sulphuretted hydrogen, and the crystallized succinic acid obtained from the filtered liquor.

Succinic acid may be also produced by the action of hot concentrated nitric acid upon *stearic acid*; a clear solution is thus obtained, which is to be concentrated by evaporation, and agitated with warm water to separate undecomposed oily matter; the clear liquor is then again evaporated, and warm water again added; in this way the undecomposed stearic acid is separated, and the aqueous liquor, which contains the succinic acid, may then be evaporated to dryness, and the residue subjected to careful sublimation in a long-necked flask; succinic acid sublimes, and leaves (the less volatile?) suberic acid; or if suberic acid rises with it, it may be separated by solution and crystallization, suberic acid being less soluble than succinic.

When succinic acid, as obtained by crystallization from its aqueous solution, is subjected to repeated sublimations, it gradually passes into the *anhydrous acid*, which, however, may be directly obtained by distilling the crystallized acid with anhydrous phosphoric acid. Anhydrous succinic acid fuses at  $295^{\circ}$ , and boils at about  $480^{\circ}$ ; exposed to a humid atmosphere it gradually resumes 1 atom of water; it is less easily soluble in water, and more so in alcohol, and in ether, than the hydrated acid. It consists, according to D'Arcet, of

|                              | D'Arcet. |      |    |      |     |      | Berzelius. |             |
|------------------------------|----------|------|----|------|-----|------|------------|-------------|
| Carbon.....                  | 4        | .... | 24 | .... | 48  | .... | 48.14      | .... 47.600 |
| Hydrogen .....               | 2        | .... | 2  | .... | 4   | .... | 4.05       | .... 4.512  |
| Oxygen .....                 | 3        | .... | 24 | .... | 48  | .... | 47.81      | .... 47.888 |
| <hr/>                        |          |      |    |      |     |      |            |             |
| Anhydrous succinic acid..... | 1        |      | 50 |      | 100 |      | 100.00     | 100.000     |

When the hydrate of succinic acid is heated to between  $270^{\circ}$  and  $285^{\circ}$ , it gradually loses half of its water, and sublimes in white acicular

crystals, which are more difficultly soluble in water and in alcohol than the hydrated acid; they fuse at  $320^{\circ}$ , and boil at about  $470^{\circ}$ , but they are volatile at  $285^{\circ}$ . The components of this form of the acid may be represented as

|                            |   |      |     |      |        |      |                   |
|----------------------------|---|------|-----|------|--------|------|-------------------|
| Carbon .....               | 8 | .... | 48  | .... | 44.04  | .... | D'Arcet.<br>44.15 |
| Hydrogen .....             | 5 | .... | 5   | .... | 4.59   | .... | 4.80              |
| Oxygen .....               | 7 | .... | 56  | .... | 51.37  | .... | 51.05             |
| <hr/>                      |   |      |     |      |        |      |                   |
| Sublimed succinic acid.... | 1 |      | 109 |      | 100.00 |      | 100.00            |

The *hydrated*, or *crystallised acid*, as obtained from its aqueous solution, forms small prisms, and rhombic and hexangular tables; according to Dumas, it is soluble in between 5 and 6 parts of cold, and 2 and 3 of boiling water; but according to Berzelius and Löwig it requires 25 of cold and 3 of boiling water for solution. It is difficultly soluble in cold alcohol and ether, but boiling alcohol and ether dissolve it more readily. Its equivalent is 59; its ultimate composition, according to Liebig and Wöhler, Bromeis, D'Arcet, and Ronalds, is

|                                 |   |      |    |      |        |      |                   |      |                  |
|---------------------------------|---|------|----|------|--------|------|-------------------|------|------------------|
| Carbon .....                    | 4 | .... | 24 | .... | 40.68  | .... | Bromeis.<br>40.59 | .... | D'Arcet.<br>41.1 |
| Hydrogen .....                  | 3 | .... | 3  | .... | 5.08   | .... | 5.15              | .... | 5.0              |
| Oxygen .....                    | 4 | .... | 32 | .... | 54.24  | .... | 54.26             | .... | 53.9             |
| <hr/>                           |   |      |    |      |        |      |                   |      |                  |
| Crystallised succinic acid .... | 1 |      | 59 |      | 100.00 |      | 100.00            |      | 100.0            |

Succinic acid is especially distinguished from benzoic acid, by being almost insoluble in oil of turpentine. It is remarkable for its indestructibility by powerful chemical agents; it is neither decomposed by chlorine, nor by nitric acid. When fused with excess of caustic potassa it yields oxalic acid, and inflammable gas. (LIEBIG and WÖHLER.) When *succinate of lime* is subjected to dry distillation, carbonic acid and inflammable gases are evolved, and an empyreumatic oil passes over, which, when rectified, yields *succinone*, a colorless oily liquid. (D'ARCT.)

The substances chiefly employed for the falsification of this acid, are, according to Dumas, tartaric acid, bisulphate of potassa, and sal-ammoniac: tartaric acid is discovered by the carbonaceous residue which it leaves when heated; the sulphate, by its want of volatility; and sal-ammoniac, by the odor of ammonia which it gives out when rubbed with lime.

When the vapor of anhydrous sulphuric acid is passed over succinic acid, care being taken to avoid elevation of temperature during the action, a part of the succinic acid combines with the sulphuric, to form *sulpho-succinic acid* =  $C_8H_3O_5, 2SO_3, + 3H_2O$ . (FEHLING. See also BERZELIUS, in respect to the composition and combinations of this acid. *Lehrbuch*, i. 736.)

*Succinates.* Succinic acid is among the more powerful organic acids. The soluble succinates produce a yellowish-red precipitate in solutions of the neutral and basic salts of peroxide of iron, and have therefore been employed in the separation of the oxides of iron and manganese. When the insoluble succinates are heated in a glass tube with bisulphate of potassa, they yield a sublimate of succinic acid. Succinic acid forms neutral and acid salts with the alkaline bases, and basic and neutral salts



with the oxides of the heavy metals. The soluble succinates have the peculiar flavor of the acid. These salts have been chiefly examined by Fehling and by Döpping. (*Ann. der Pharm.*, xxxviii. 285 ; xlvii. 253 ; xlix. 154 and 350.)

*Succinate of Ammonia*,  $\text{NH}_4\text{O}, \overline{\text{Suc}}$ , is obtained by supersaturating succinic acid by a strong solution of ammonia, and evaporating *in vacuo* over quicklime ; it forms prismatic crystals, having a slightly acid reaction, and very soluble in water and in alcohol ; they do not effloresce, but when exposed to air they lose ammonia and pass into the acid salt. The solution of succinate of ammonia is occasionally used as a precipitant of oxide of iron. The ultimate components of this salt are

|                      |   |      |    |      |        | Döpping.   | Fehling.     |
|----------------------|---|------|----|------|--------|------------|--------------|
| Carbon .....         | 4 | .... | 24 | .... | 31.58  | .... 31.76 | .... 31.94   |
| Hydrogen .....       | 6 | .... | 6  | .... | 7.89   | .... 7.83  | .... 7.92    |
| Oxygen.....          | 4 | .... | 32 | .... | 42.10  | .... 41.87 | } .... 60.14 |
| Nitrogen .....       | 1 | .... | 14 | .... | 18.43  | .... 18.54 |              |
| <hr/>                |   |      |    |      |        |            |              |
| Succinate of ammonia | 1 |      | 76 |      | 100.00 | 100.00     | 100.00       |

*Bisuccinate of Ammonia*.  $\text{NH}_4\text{O}, \text{HO}, 2\overline{\text{Suc}}$ . When the neutral succinate and succinic acid are dissolved in water, in single equivalent proportions, six-sided prismatic crystals are obtained on evaporation, which are acid, permanent in the air, and readily soluble in water and in alcohol. When this salt is subjected to a temperature of  $285^\circ$ , it is resolved into *bisuccinamide* and water.

*Bisuccinamide*,  $[\text{NH}, \text{C}_4 \text{H}_2 \text{O}] \text{C}_4 \text{H}_2 \text{O}_3 = \text{NH}, 2[\text{C}_4 \text{H}_2 \text{O}_2]$  was formed by D’Arcet by acting upon anhydrous succinic acid by dry ammonia ; but according to Fehling it may be best obtained by sublimation from the bisuccinate of ammonia as just stated ; in which case  $\text{NH}_3, 2[\text{C}_4 \text{H}_2 \text{O}_3] = [\text{NH}, \text{C}_4 \text{H}_2 \text{O}] \text{C}_4 \text{H}_2 \text{O}_3, + 2\text{HO}$ . This compound is more soluble in water than in alcohol or ether ; it may be purified by crystallization from its aqueous solution, in which case the crystals contain 2 atoms of water, which they lose when dried at  $212^\circ$ . Boiled in a solution of potassa, they evolve ammonia and form succinate of potassa, and when digested with oxide of lead, a compound with that oxide is formed. (FEHLING.) Anhydrous bisuccinamide consists of

|                         |        |      |    |      |        | Fehling.   |
|-------------------------|--------|------|----|------|--------|------------|
| Carbon .....            | 8      | .... | 48 | .... | 48.48  | .... 48.84 |
| Hydrogen.....           | 5      | .... | 5  | .... | 5.06   | .... 5.33  |
| Oxygen.....             | 4      | .... | 32 | .... | 32.32  | .... 31.21 |
| Nitrogen .....          | 1      | .... | 14 | .... | 14.14  | .... 14.62 |
| <hr/>                   |        |      |    |      |        |            |
| Anhydrous bisuccinamide | .... 1 |      | 99 |      | 100.00 | 100.00     |

When *succinic ether* is agitated for a long time with solution of ammonia, a white precipitate is formed, which, washed with alcohol, and dissolved in boiling water, yields, on cooling, acicular crystals of *succinamide*,  $= \text{NH}_2, \text{C}_4 \text{H}_2 \text{O}_2$ . When suddenly heated up to  $572^\circ$ , succinamide is resolved into ammonia and bisuccinamide.  $2[\text{NH}_2, \text{C}_4 \text{H}_2 \text{O}_2] = [\text{NH}, \text{C}_4 \text{H}_2 \text{O}] \text{C}_4 \text{H}_2 \text{O}_3 + \text{NH}_3$ . Fehling’s analysis of succinamide gives

|                   |   |      |    |      |        | Fehling.   |
|-------------------|---|------|----|------|--------|------------|
| Carbon.....       | 4 | .... | 24 | .... | 41·38  | .... 41·71 |
| Hydrogen .....    | 4 | .... | 4  | .... | 6·94   | .... 6·97  |
| Oxygen .....      | 2 | .... | 16 | .... | 27·56  | .... 27·20 |
| Nitrogen .....    | 1 | .... | 14 | .... | 24·12  | .... 24·12 |
| <hr/>             |   |      |    |      |        |            |
| Succinamide ..... | 1 |      | 58 |      | 100·00 | 100·00     |

*Succinate of Potassa*;  $\text{KO}, \overline{\text{Suc}}$ ; crystallizes, according to Fehling, out of its neutral solution, in small rhombic tables resembling chlorate of potassa, easily soluble in water and in diluted alcohol; not altered in the air; and being  $2[\text{KO}, \overline{\text{Suc}}] + \text{HO}$ . The mother-liquor yields another salt, in indistinct crystals, which, though not deliquescent, absorb moisture. According to Döpping, succinate of potassa deposited from its concentrated solution, is an imperfectly crystallizable, deliquescent salt, soluble in alcohol, but insoluble in ether, and containing 2 atoms of water, which it loses at  $212^\circ$ . At  $390^\circ$  it fuses and is decomposed.

*Bisuccinate of potassa*,  $[\text{KO}, \text{HO}, 2\overline{\text{Suc}}, + 4\text{HO},]$  forms prismatic crystals, which at  $212^\circ$  lose 4 atoms of water. When 1 atom of this salt is dissolved in hot water with 2 atoms of succinic acid, crystals of a *quadri-succinate of potassa* are deposited on cooling,  $= \text{KO}, 4\overline{\text{Suc}}, 5\text{HO}$ .

*Succinate of Soda*;  $\text{NaO}, \overline{\text{Suc}} + 6\text{HO}$ ; forms efflorescent tabular crystals, which are anhydrous after having been dried at  $212^\circ$ . *Bisuccinate of soda*,  $[\text{NaO}, 2\overline{\text{Suc}} + 6\text{HO},]$  forms tabular crystals, which may be obtained large and well defined. This salt sometimes crystallizes with only 4 atoms of water.

*Succinate of Lime*.  $\text{CaO}, \overline{\text{Suc}}$ . When cold solutions of chloride of calcium and succinate of soda are mixed, a crystalline precipitate gradually ensues of  $\text{CaO}, \overline{\text{Suc}} + 3\text{HO}$ , which becomes anhydrous when dried at  $392^\circ$ . If the solutions are at their boiling temperatures, the precipitate is almost immediately produced, and consists of fine needles,  $= \text{CaO}, \overline{\text{Suc}}, + \text{HO}$ . When finely pulverised carbonate of lime is digested in a solution of succinic acid, heated to about  $130^\circ$ , crystals of *bisuccinate of lime* separate as the liquor cools  $= \text{CaO}, \text{HO}, 2\overline{\text{Suc}} + 2\text{HO}$ . This salt is also formed when the neutral succinate is warmed in very dilute nitric acid; it crystallizes as the liquor cools. When dried at  $212^\circ$ , it loses its 2 atoms of water of crystallization, and is then  $\text{CaO}, \text{HO}, 2\overline{\text{Suc}}$ . (FEHLING.)

*Succinate of Baryta*.  $\text{BaO}, \overline{\text{Suc}}$ . When saturated solutions of chloride of barium and succinate of soda are mixed, a precipitate of succinate of baryta immediately ensues: if the solutions be dilute, it is only gradually formed, and is then in crystalline grains. This salt is anhydrous, and is very slightly soluble in water, but readily soluble in hydrochloric and in nitric acid.

*Succinate of Strontia*,  $\text{SrO}, \overline{\text{Suc}}$ , resembles the barytic salt, and is also anhydrous.

*Succinate of Magnesia*;  $\text{MgO}, \overline{\text{Suc}}$ ; crystallizes with different proportions of water. When a hot solution of succinic acid is saturated by carbonate of magnesia, crystals separate on cooling, which contain 6 atoms of water; they are permanent in the air, soluble in water, and insoluble



in alcohol. When dried at  $268^{\circ}$ , they become anhydrous. A moderately strong solution of this salt yields crystals with 5 atoms of water, 4 of which are expelled at  $212^{\circ}$ , and the remaining atom at  $390^{\circ}$ . A very concentrated solution of the same salt gradually concretes into a hard crystalline mass, containing also 5 or  $5\frac{1}{2}$  atoms of water. Fehling also obtained crystals with 6 atoms of water. When a solution of neutral succinate of magnesia is decomposed by ammonia, a white pulverulent precipitate falls, which is insoluble in water, alcohol, and acetic acid,  $= 6\text{MgO}, 2\overline{\text{Suc}}, 3\text{HO}$ . (DÖPPING.)

*Succinate of Manganese*,  $\text{MnO}, \overline{\text{Suc}}, + 4\text{HO}$ , crystallizes in permanent amethystine prisms, from a solution of carbonate of manganese in hot succinic acid. This salt is insoluble in alcohol, and loses the whole of its water at  $212^{\circ}$ .

*Succinate of Protoxide of Iron*;  $\text{FeO}, \overline{\text{Suc}}$ ; is a greenish powder, difficultly soluble in water, and in excess of succinic acid. Döpping has described two *succinates of peroxide of iron*, represented by the formulæ  $\text{Fe}_2\text{O}_3, 2\overline{\text{Suc}}$ , and  $9[\text{Fe}_2\text{O}_3] + \overline{\text{Suc}}$ ; the normal salt  $= \text{Fe}_2\text{O}_3, 3\overline{\text{Suc}}$ , has not been obtained. The first compound, containing 1 atom of the oxide and 2 of the acid, is formed when a solution of sesquichloride of iron is decomposed by neutral succinate of potassa, and the red gelatinous precipitate washed first with water, then with a solution of sal-ammoniac, and lastly with alcohol. It is insoluble in water and in alcohol, very sparingly soluble in succinic acid, but soluble in acetic acid, especially when heated. It dries into a brown brittle mass. When digested in aqueous ammonia, it loses its gelatinous character and becomes  $9[\text{Fe}_2\text{O}_3] + \overline{\text{Suc}}$ .

*Succinate of Zinc*;  $\text{ZnO}, \overline{\text{Suc}}$ ; forms a white crystalline anhydrous powder, difficultly soluble in water, and insoluble in alcohol. It is obtained by gradually adding freshly precipitated carbonate of zinc to a boiling solution of succinic acid, care being taken to leave the latter in excess.

*Succinate of Nickel*.  $\text{NiO}, \overline{\text{Suc}}, + 4\text{HO}$ . This salt is prepared by dissolving freshly precipitated oxide of nickel in a warm solution of succinic acid, and evaporating the pale-green solution over sulphuric acid *in vacuo*: clusters of green crystals are formed, soluble in water, acetic acid, and ammonia, but insoluble in alcohol: they are rendered anhydrous by drying at  $212^{\circ}$ . (DÖPPING.)

*Succinate of Copper*;  $\text{CuO}, \overline{\text{Suc}}$ ; may be obtained as the zinc salt; it is a crystalline powder, very little soluble either in water, or in excess of succinic acid: it is anhydrous.

*Succinate of Lead*;  $\text{PbO}, \overline{\text{Suc}}$ ; falls in the form of a white crystalline precipitate, on adding succinic acid or succinate of potassa to a solution of acetate of lead; it is very little soluble in water and in acetic acid.

When warm solutions of subacetate of lead and succinate of soda are mixed, a plastic precipitate falls, which may be kneaded in warm, but which becomes hard and brittle in cold water. It consists, according to Döpping, of  $3\text{PbO}, 2\overline{\text{Suc}}$ . Fehling found that when this precipitate is boiled in the solution in which it is formed, a part is redissolved, and when the liquor is set aside for some months in a stopped bottle, it deposits

long acicular crystals,  $= 3\text{PbO}, 2\overline{\text{Suc}}, 2\text{HO}$ . When the neutral succinate of lead is digested in excess of a solution of ammonia, a white insoluble powder remains, being, according to Döpping,  $3\text{PbO}, \overline{\text{Suc}}$ .

*Succinate of Mercury.* When a solution of nitrate of black oxide of mercury is mixed with succinate of soda, a white insoluble precipitate falls, being, according to Döpping, a mixture of basic nitrate and succinate of the oxide. Succinic acid occasions no precipitate in solution of corrosive sublimate, nor does succinate of soda; but a mixture of the saturated solutions gradually deposits slender silky crystals which are composed of corrosive sublimate and succinate of soda. When freshly precipitated red oxide of mercury is boiled with a solution of succinic acid, a white basic salt is after a time deposited.

*Succinate of Silver.*  $\text{AgO}, \overline{\text{Suc}}$ . Succinate of soda throws down a white pulverulent precipitate from nitrate of silver, which is very sparingly soluble in water and in acetic acid; it is anhydrous, and consists of

|                           |   |      |     |      |        | Döpping.   |
|---------------------------|---|------|-----|------|--------|------------|
| Oxide of silver .....     | 1 | .... | 116 | .... | 69.88  | .... 69.91 |
| Succinic acid .....       | 1 | .... | 50  | .... | 30.12  | .... 30.09 |
| <hr/>                     |   |      |     |      |        |            |
| Succinate of silver ..... | 1 |      | 166 |      | 100.00 | 100.00     |

XXVII. SUBERIC ACID.  $\text{C}_8\text{H}_6\text{O}_3, + \text{HO} = \overline{\text{Sub}}, \text{HO}$ . This acid was originally obtained by the action of nitric acid upon *cork*, by Brugnatelli, (*Crell's Annals*, 1787, i. 154); it was afterwards examined by Bouillon la Grange (*Ann. de Chimie*, xxiii. 42), by Chevreul (*Ann. Ch. et Ph.*, lxii. 323, and *Nicholson's Journ.*, xxiii. 149), by Brandes, in 1821 and 1822, (*Schweigger's Jarhbuch*, ii. 393, iii. 83, and vi. 282), and by Bussy (*Journ. der Pharm.*, viii. 110, and xix. 425). The acid may be obtained as follows: 1 part of rasped cork is digested in a retort, with 6 parts of nitric acid, sp. gr. 1.26, as long as nitric oxide is evolved; and the acid which distils over is repeatedly returned into the retort. The cork swells, whitens, and gradually dissolves, and a fused fatty matter at the same time collects upon the surface of the liquor. When the action is over, the liquor is evaporated in a porcelain basin by a gentle heat, or in a water-bath, and constantly stirred, till it acquires the consistence of thin honey; it is then largely diluted with boiling water, and digested for some time, when a waxy substance separates upon the surface, and an insoluble matter falls. The liquor is then allowed to cool, filtered, and gently evaporated, till, on cooling, it deposits the suberic acid, and crystals of oxalic acid are generally at the same time formed. The pulverulent acid is then dissolved in a little boiling water, and the hot solution filtered, when it deposits suberic acid on cooling. It sometimes contains a little oxalate of lime, which may be separated by dissolving it in caustic ammonia, from which the suberic acid may be precipitated by another acid; or it may be purified by careful sublimation. (CHEVREUL. BRANDES.)

Suberic acid is also formed by the action of nitric acid upon the fat acids of tallow. The *stearic acid* as prepared for candles may be used for this purpose; it is boiled in a retort with 3 parts of nitric acid; in about half an hour the action becomes very violent, and caution is required to prevent boiling over, but afterwards there is less evolution of



gas, and more nitric acid may be added and the boiling continued; at last the distillation goes on quietly, and the acid which passes over may be from time to time returned into the retort, till the whole of the fatty matter has disappeared. The liquor is then distilled, till about one-half of it has passed over, and the remainder, on being left in a cold place, concretes into a mixture of succinic and suberic acid, which is let drain in a funnel, and washed with a very little cold water, when the suberic acid remains. It may be dissolved in the least possible quantity of boiling water, from which it separates on cooling. This acid may be rendered perfectly pure by washing it with cold ether, and then boiling it for some hours in dilute nitric acid, from which it separates on cooling. (LAURENT.) Tilley and Bromeis also obtained suberic acid by the action of nitric acid upon castor oil.

Suberic acid, as it separates from its aqueous solution, is a white powder; it fuses (when obtained by the last process) at about  $250^{\circ}$ , without losing weight; but Brandes places its point of fusion (when obtained from cork) much lower. On cooling, it concretes into an acicular crystalline mass. It sublimes, when heated above its fusing-point in a retort, and condenses in oily drops which concrete on cooling. Heated in the air, it evolves irritating fumes, and condenses on cold substances in long needles; but these sublimations can seldom be effected without more or less decomposition, and deposition of charcoal. Suberic acid is soluble in about 2 parts of boiling water, but it requires as much as 100 parts of water at  $45^{\circ}$  for its solution. It is soluble in between 4 and 5 parts of absolute alcohol at  $50^{\circ}$ , and in about 10 parts of ether, at the same temperature. 87 parts of boiling alcohol dissolve 100 of suberic acid, and 6 parts of boiling ether dissolve 1 part. It is readily soluble in oil of turpentine, and mixes in all proportions with the fat oils when heated in them. (BOUILLON LA GRANGE.)

*Anhydrous suberic acid*, as it exists in combination with bases, consists of

|                             |   |      |    |      |       | Bussy.     |
|-----------------------------|---|------|----|------|-------|------------|
| Carbon .....                | 8 | .... | 48 | .... | 61.5  | .... 61.99 |
| Hydrogen .....              | 6 | .... | 6  | .... | 7.7   | .... 7.59  |
| Oxygen .....                | 3 | .... | 24 | .... | 30.8  | .... 30.42 |
| <hr/>                       |   |      |    |      |       |            |
| Anhydrous suberic acid .... | 1 |      | 78 |      | 100.0 | 100.00     |

The *hydrated or crystallized acid* is composed of

|                                  |   |      |    |      |        | Bussy.     | Boussingault. | Laurent.   | Bromeis.   |
|----------------------------------|---|------|----|------|--------|------------|---------------|------------|------------|
| Carbon .....                     | 8 | .... | 48 | .... | 55.17  | .... 55.78 | .... 55.1     | .... 55.55 | .... 55.09 |
| Hydrogen.....                    | 7 | .... | 7  | .... | 8.04   | .... 7.98  | .... 8.0      | .... 8.10  | .... 7.94  |
| Oxygen.....                      | 4 | .... | 32 | .... | 36.79  | .... 36.24 | .... 36.9     | .... 36.35 | .... 36.97 |
| <hr/>                            |   |      |    |      |        |            |               |            |            |
| Crystallized }<br>suberic acid } | 1 |      | 87 |      | 100.00 | 100.00     | 100.0         | 100.00     | 100.00     |

*Suberates.* The salts of the suberic acid have a saline and slightly acid taste; they are precipitated by acids, and decomposed at a red heat, when a part of the acid generally sublimes. They are either obtained directly or by double decomposition.

*Suberate of Ammonia*,  $\text{NH}_4 \text{O}, \overline{\text{Sub}}$ , crystallizes in slender 4-sided prisms, volatile, and very soluble in water. *Suberate of potassa* forms clustered crystals, readily soluble, slightly deliquescent, and fusible before

decomposition. *Suberate of soda* forms 4-sided prisms; it is soluble in its weight of water, and absorbs moisture from the air. *Suberate of lime* is pulverulent; it is soluble in 40 of cold and 9 of boiling water. Subjected to dry distillation, it yields *suberone* =  $C_8H_7O$ . (BOUSSINGAULT. TILLEY.) *Suberate of baryta* is pulverulent, and soluble in 70 of cold and 16 of boiling water. *Suberate of strontia* resembles the baryta-salt, but is more soluble. *Suberate of magnesia* is a very soluble uncrystallizable salt. *Suberate of manganese* is soluble and difficultly crystallizable. *Suberate of ammonia* produces a white precipitate in solutions of the *protosalts of iron*, and in the salts of *zinc*, and a brown precipitate in the *persalts of iron*. The suberates of *cobalt*, *copper*, and *uranium* are respectively red, green, and yellow, and are insoluble. *Suberate of lead* is a white precipitate =  $PbO$ , Sub: when digested in a solution of subacetate of lead it passes into  $3 PbO$ , Sub. *Suberate of silver* is a white precipitate, =  $AgO$ , Sub. (BROMEIS.)

XXVIII. MELLITIC ACID.  $C_4H_4O_4$ , or  $C_4O_3 + HO$ , or  $C_4O_4 + H$ . This acid has hitherto only been found in a very rare mineral, the *Mellite*, or *Honeystone*, which is a *mellitate of alumina*. It has not as yet been artificially formed, as is the case with the succinic acid, but its composition and origin give it a place amongst the organic acids.

*Mellite* has hitherto only been found in small solitary octohedral crystals of a honey-yellow color, among the layers of wood coal, at Artern, in Thuringia, and appears to have been regarded as amber, till Werner, in 1790, pointed out its peculiarities, and termed it *honigstein*. Its composition was determined by Klaproth, in 1797, (*Beiträge*), and the mellitic acid has since been more particularly studied by Wöhler, and by Liebig and Pelouze. (*Ann. der Pharm.*, xix. 352; *Ann. Ch. et Ph.*, 3ème Serie, ii. 69.)

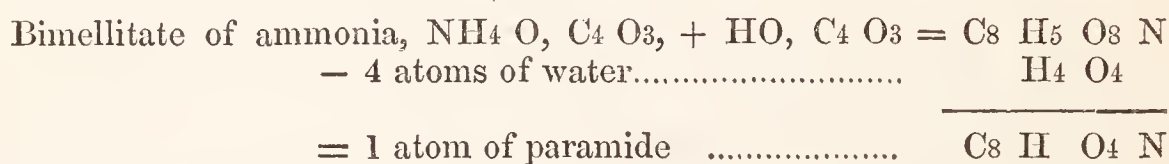
Mellitic acid is obtained by digesting the pulverised mineral in a boiling solution of carbonate of ammonia, which throws down alumina, and forms a mellitate of ammonia; as this is acid, and retains a little alumina in solution, it requires to be neutralised by ammonia, and filtered. The clear liquor, on evaporation, yields crystals, which must be purified by repeated crystallization, and their solution then precipitated by acetate of lead; the resulting *mellitate of lead* decomposed by sulphuretted hydrogen, yields a solution of mellitic acid, which, filtered, evaporated to the consistence of syrup, and then left to spontaneous evaporation, yields a crystalline mass of the acid. The ammonia-salt may also be decomposed by nitrate of silver, the resulting mellitate of silver decomposed by dilute hydrochloric acid, and the remaining solution evaporated, when any excess of hydrochloric acid goes off, and the remaining liquor yields the mellitic acid.

This acid crystallizes in delicate white prisms, is very sour, not altered by the air, and may be heated to above  $500^\circ$  without decomposition. At a higher temperature it fuses, burns, and exhales an aromatic odor, leaving much charcoal. By dry distillation a small part sublimes, but it is chiefly decomposed. It is readily soluble in water, and its concentrated solution is a long time in crystallizing. It dissolves in cold alcohol, and crystallizes when this solution is left to spontaneous evaporation. It is not decomposed even by boiling sulphuric or nitric acid, and is insoluble

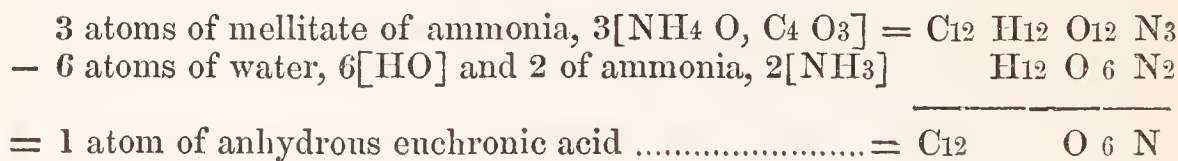


in the latter. The general formula of the salts of this acid is  $\text{MO}, \text{C}_4 \text{H O}_4$ ; but the salt of silver, which originally is  $\text{AgO}, \text{C}_4 \text{H O}_4$ , when dried at  $212^\circ$ , loses an atom of water, and becomes  $\text{AgO}, \text{C}_4 \text{O}_3$ , which is equivalent to  $\text{Ag}, \text{C}_4 \text{O}_4$ ; in which case, the *radical* of the salt is isomeric with carbonic oxide, being in fact  $= 4\text{CO}$ .

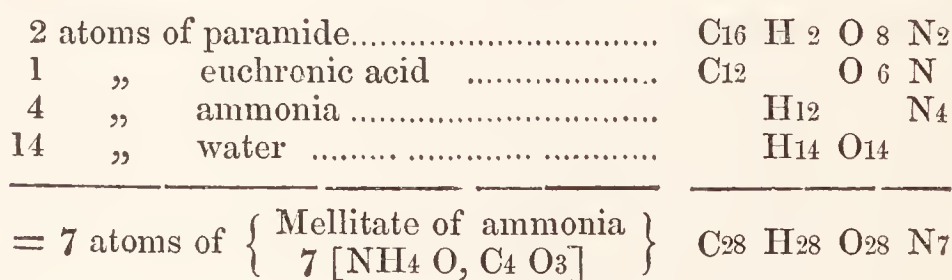
When *mellitate of ammonia*, which is  $\text{NH}_3, \text{C}_4 \text{H O}_4$ , or  $\text{NH}_4 \text{O}, \text{C}_4 \text{O}_3$ , is heated in a retort to  $320^\circ$ , it gives off ammonia and water, and two new compounds remain, one of which is soluble, and contains *euchronic acid* in combination with ammonia; the other is an insoluble yellow substance, and has been named *paramide*; when it is long boiled with water, it is converted into *bimellitate of ammonia*: its composition, which is  $\text{C}_8 \text{H O}_4, \text{N}$ , explains its formation, and conversion into bimellitate; for if we subtract 4 atoms of water from bimellitate of ammonia, we form paramide, and the resumption of the elements of 4 atoms of water by paramide, reconverts it of course into the bimellitate.



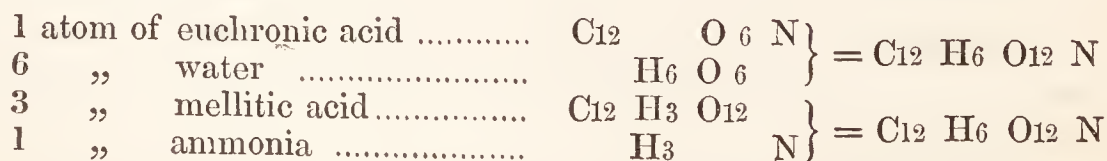
When hydrochloric acid is added to the euchronate of ammonia, the euchronic acid is deposited in the form of a white crystalline powder  $= \text{C}_{12} \text{O}_6 \text{N} + 2\text{HO}$ , or  $\text{C}_{12} \text{H}_2 \text{O}_8 \text{N}$ ; it appears therefore that (anhydrous) euchronic acid is formed by the subtraction of 6 atoms of water and 2 of ammonia from 3 of mellitate of ammonia.



It would further appear that the following substances are produced by the action of heat upon 7 atoms of mellitate of ammonia.



When euchronic acid is boiled with water, it becomes converted into mellitic acid and ammonia.



When euchronic acid is acted upon by a plate of zinc, it yields a deep blue powder, which, dissolved in potassa or ammonia, furnishes a fine purple liquor; this blue powder appears to be an inferior oxide of the same radical, which, combined with more oxygen, forms euchronic acid.

“The whole subject of mellitic and euchronic acid is most interesting, but mellitic acid is so rare, that it is very difficult to find material for the investigation. As mellitic acid, like succinic acid, is of organic origin,

and contains only 1 equivalent of hydrogen less, and 1 of oxygen more, than succinic acid, we may hope to be enabled to obtain it artificially." (GREGORY, *Outlines*, 282.)

XXIX. CAHINCIC ACID. Under this name Pelletier and Caventou (*Ann. Ch. et Ph.*, xliv. 291) have described an acid procured from the cortical part of the *cahinca* root; the plant (*Chiococca racemosa*) belongs to the *Rubiaceæ*, and grows in Brazil, being used for the cure of intermittents, dropsy, and other diseases. The acid is obtained by dropping hydrochloric acid into a decoction of the root; it is gradually deposited in small crystals. It is more perfectly procured by evaporating a strong alcoholic tincture of the cahinca root to dryness, dissolving the residue in water, precipitating by lime, and decomposing the calcareous salt which falls, by boiling it in an alcoholic solution of oxalic acid: the cahincic acid must then be purified by recrystallization.

Cahincic acid requires 600 parts of water for its solution; it is very soluble in alcohol, and the solution, if saturated when hot, deposits the acid in tufts of crystals as it cools. Ether dissolves it as sparingly as water. It is intensely bitter: when heated, it softens, chars, and yields a white crystalline sublimate, which contains no ammonia.

Cahincic acid is charred by sulphuric acid: with hydrochloric acid it forms a gelatinous compound, from which water throws down white flakes, which are not bitter: nitric and acetic acid produce very similar effects. With ammonia, potassa, lime, and baryta, it forms soluble neutral salts, which are not crystallizable, and from which the acids throw down cahincic acid. From Liebig's analysis of the crystallized acid dried at  $212^{\circ}$ , (*Ann. Ch. et Ph.*, xlvii. 186,) it appears to consist of

|                     |    |       |     |       |       |
|---------------------|----|-------|-----|-------|-------|
| Carbon .....        | 15 | ..... | 90  | ..... | 57.0  |
| Hydrogen .....      | 12 | ..... | 12  | ..... | 7.6   |
| Oxygen .....        | 7  | ..... | 56  | ..... | 35.4  |
| <hr/>               |    |       |     |       |       |
| Cahincic acid ..... | 1  |       | 158 |       | 100.0 |

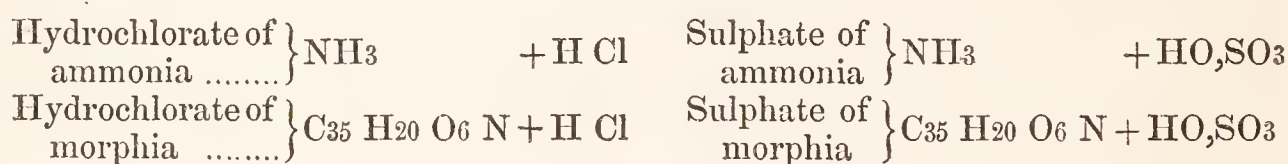
But its equivalent has not been determined by experiment, nor have any of its salts been analyzed. When acted on by the mineral acids, it first dissolves in them, and afterwards the above-mentioned gelatinous substance forms in the solution: when this product with nitric acid is boiled in the acid, a peculiar bitter substance is formed, but no oxalic acid.

## § X. VEGETABLE ALKALOIDS, AND SUBSTANCES ASSOCIATED WITH OR ALLIED TO AND DERIVED FROM THEM.

THE discovery of these substances is one of the most curious and important of modern chemistry. The first of them was detected in *opium*, in 1816, by Sertuerner, of Einbeck, near Hanover. Several others were afterwards pointed out by Pelletier and Caventou, and among them *cinchonia* and *quinia* (in different species of *cinchona*,) which have proved of so much use in medicine; more lately, several others have been added to the list. These *salifiable bases* appear all to contain *nitrogen* as one of their ultimate elements; they have a bitter taste, are for the most part very sparingly soluble in water, more soluble in alcohol, and readily soluble



in most of the dilute acids: with infusion of galls, and with excess of iodic acid, they furnish difficultly-soluble precipitates; their compounds with the acids are decomposed and precipitated by the alkalis. They are mostly crystallizable, and are represented by very high equivalent numbers. They restore the blue color to reddened litmus. They are found in plants united to certain *acids*, and usually forming neutral or acid salts, which, as well as their artificial combinations, are decomposed in the voltaic circle, and the base is evolved at the negative pole. Many hypotheses have been built upon the ultimate composition of these alkaloids, and some curious analogies pointed out respecting them by Liebig, Dumas, and others. A laborious analytical essay, having reference to the greater number of them, has been published in the *Ann. Ch. et Ph.*, (LXviii. 113) by Regnault; but till organic analysis has made further progress, and has become more independent of hypothetical views, each experimentalist will necessarily differ somewhat from his predecessors. Their optical properties have been studied by Bouchardat and by Biot. (*Ann. Ch. et Ph.*, Oct. 1843.) Graham observes that ammonia is a true type of these alkaloids, and that they unite directly with hydrochloric acid as ammonia does, without the separation of water; and that, as in the corresponding salts of ammonia, an atom of water essentially belongs to their salts with oxygen-acids. Thus, in the following formulæ, morphia,  $C_{35} H_{20} O_6 N$ , appears exactly equivalent to ammonia,  $N H_3$ .



The hydrochlorates of the vegetable bases also, he observes, resemble sal ammoniac in forming a crystallizable double salt with 1 atom of bichloride of platinum, and with 2 atoms of chloride of mercury. This similarity in properties favors the idea that these bases may have a constitution analogous to that of ammonia, or be *amides* of an unknown radical, as ammonia is the amide of hydrogen. (*Elements*, 972.)

In consequence of the analogy that pervades these principles, one general method of separating them is applicable to all, though each may require peculiar modifications of it. The substance which contains them is boiled in water acidulated by hydrochloric acid, the decoction is filtered and neutralized by ammonia, lime, or magnesia, when the alkaloid is precipitated, and afterwards separated and purified.

#### I. MORPHIA, AND THE OTHER PROXIMATE PRINCIPLES OF OPIUM, AND THEIR DERIVATIVES.

The chemical examination of *opium* has been remarkably productive in interesting results. It has led to the discovery of several alkaloids, and of a peculiar acid with which they are combined; the substances which we shall have to describe under this head being the following, viz., morphia, narcotina, codeia, narceia, meconia, thebaia, and meconic acid.

*Opium* is the inspissated milky juice which flows from incisions made in the unripe seed-capsule of the poppy; it is only effectively obtained in

warm climates, and is imported into this country chiefly from Turkey and India; it contains the above-mentioned substances, upon which its extraordinary medicinal powers depend, together with several others of little importance, such as gum, resin, extractive, ligneous matter, oil, and caoutchouc. Mulder analyzed five specimens of Smyrna opium with the following results. (THOMSON'S *Organic Chemistry*, 586, and *Pharm. Centr. Blatt.*, 1834, p. 574.)

|                  | 1            | 2            | 3             | 4            | 5            | Average.     |
|------------------|--------------|--------------|---------------|--------------|--------------|--------------|
| Narcotina .....  | 6·808        | 8·150        | 9·360         | 7·702        | 6·546        | 7·713        |
| Morphia .....    | 10·842       | 4·106        | 9·852         | 2·842        | 3·800        | 6·228        |
| Codeia .....     | 0·678        | 0·834        | 0·848         | 0·858        | 0·620        | 0·767        |
| Narceia .....    | 6·662        | 7·506        | 7·684         | 9·908        | 13·240       | 9·000        |
| Meconia .....    | 0·804        | 0·846        | 0·314         | 1·380        | 0·608        | 0·790        |
| Meconic acid ... | 5·124        | 3·968        | 7·620         | 7·252        | 6·644        | 6·121        |
| Fat .....        | 2·166        | 1·350        | 1·816         | 4·204        | 1·508        | 2·209        |
| Caoutchouc ...   | 6·012        | 5·026        | 3·674         | 3·754        | 3·206        | 4·338        |
| Resin .....      | 3·582        | 2·028        | 4·112         | 2·208        | 1·834        | 2·753        |
| Gummy extract    | 25·200       | 31·470       | 21·834        | 22·606       | 25·740       | 25·370       |
| Gum .....        | 1·042        | 2·896        | 0·698         | 2·998        | 0·896        | 1·706        |
| Mucilage .....   | 19·086       | 17·098       | 21·064        | 18·496       | 18·022       | 18·733       |
| Water .....      | 9·846        | 12·226       | 11·422        | 13·044       | 14·002       | 12·108       |
|                  | <hr/> 97·852 | <hr/> 97·504 | <hr/> 100·858 | <hr/> 97·252 | <hr/> 96·666 | <hr/> 97·836 |

Schindler gives the following comparative results of the analyses of opium from three different places. (*Pharm. Centr. Blatt.*, 1834, p. 950.)

|  | Smyrna.      | Constantinople. | Egypt.       |
|--|--------------|-----------------|--------------|
| Morphia .....  | 10·30        | 4·50            | 7·00         |
| Codeia .....   | 0·25         | 0·52            |              |
| Meconia .....  | 0·08         | 0·30            |              |
| Narcotina .....  | 1·30         | 3·47            | 2·68         |
| Narceia .....  | 0·71         | 0·42            |              |
| Meconic acid .....   | 4·70         | 4·38            |              |
| Resin .....  | 10·93        | 8·10            |              |
| Lime .....   | 0·40         | 0·02            |              |
| Magnesia .....   | 0·07         | 0·40            |              |
| Alumina, oxide of iron, silica, and phosphate }<br>of lime ..... | 0·24         | 0·22            |              |
| Salts and volatile oil .....                                     | 3·60         | 3·60            |              |
| Mucilage, caoutchouc, fat, and lignine .....                     | 26·25        | 17·18           |              |
| Brown acid, soluble in alcohol and water .....                   | 1·04         | 0·40            |              |
| Brown acid only soluble in water, gum, and }<br>loss .....       | 40·13        | 56·49           |              |
|  | <hr/> 100·00 | <hr/> 100·00    | <hr/> 100·00 |

1. MORPHIA.  $C_{35}H_{20}O_6N + 2HO = Mor + 2HO$ . The first step in the process for extracting morphia and the other alkaloids, consists in cutting the opium into small pieces, and digesting it in distilled water at the temperature of about  $100^{\circ}$ , till its soluble parts are completely extracted: it affords a clear brown infusion, smelling strongly of opium, and *acid* to tests. There are many modes of separating the morphia from it, but among them the following are generally employed:—

*a.* Milk of lime, prepared with a quantity of lime equal to the fourth part of the weight of the opium, is added to a concentrated infusion of opium, and the mixture boiled and filtered while hot through linen; the



hot filtrate is then mixed with excess of sal-ammoniac, by which morphia is precipitated, and may be purified as described below. (MOHR, *Ann. der Pharm.*, xxxv. 122.)

b. "The following method succeeds well upon a small scale, and will serve to give the student some idea of a process very commonly pursued, when it is desired to isolate at once an insoluble organic base, and the acid with which it is in combination. A filtered solution of opium in tepid water is mixed with acetate of lead in excess; the precipitated meconate of lead is separated by a filter, and through the solution, containing acetate of morphia, now freed to a considerable extent from color, a stream of sulphuretted hydrogen is passed. The filtered, and nearly colorless liquid, from which the lead has thus been removed, may be warmed to expel the excess of gas, once more filtered, and then mixed with a slight excess of caustic ammonia, which throws down the morphia and narcotine; these may be separated by boiling ether, in which the latter is soluble. The meconate of lead, well washed, suspended in water, and decomposed by sulphuretted hydrogen, yields solution of meconic acid." (FOWNES.)

c. Upon the large scale, morphia and its salts are frequently prepared by *Gregory's process*, which is as follows: A concentrated aqueous infusion of opium is mixed with solution of chloride of calcium, which is added in slight excess. On standing, especially if warmed, the mixture deposits a copious brownish-grey precipitate of mixed meconate and sulphate of lime (the morphia being in the opium partly as meconate and partly as sulphate,) while hydrochlorate of morphia remains in solution, with a very large proportion of dark-brown coloring matter. The brown solution is evaporated till, on cooling, the hydrochlorate crystallizes, forming a nearly solid mass, which is subjected to very strong pressure in flannel. A thick viscid nearly black mother-liquor is thus expressed, which contains all the narcotine and coloring matter. The squeezed cake of hydrochlorate of morphia is of a fawn-color. It is redissolved in hot water, filtered, if necessary, and recrystallized, so much water being used that, on cooling, a semi-solid mass is obtained. This is again squeezed out, and if the squeezed cake is not quite white, it is only necessary to repeat the operation. A little animal charcoal in the second, or better still in the third crystallization, assists in removing the last traces of color. The second and third mother-liquors, although colored, are not to be thrown away, but should be added to the solution of a fresh portion of opium, so that the small quantity of hydrochlorate which is retained in solution shall not be lost. In crystallizing hydrochlorate of morphia, the liquid should always be acidulated with hydrochloric acid (after the animal charcoal is separated), because very little is then retained in solution. The purified hydrochlorate, which still contains about one-thirtieth of codeia, is now dissolved in hot water, and supersaturated with ammonia; on cooling, the morphia is deposited as a snow-white crystalline powder, which may be crystallized by means of hot alcohol. The codeia remains in the mother-liquor. 1 pound of good opium yields an ounce and a-half of hydrochlorate of morphia. (GREGORY, *Outlines*, 483.)

d. The process of the *London Pharmacopœia* is as follows:—"Take of opium, sliced, 1 pound; crystals of chloride of lead, 2 ounces, or as



much as may be sufficient; purified animal charcoal,  $3\frac{1}{2}$  ounces; hydrochloric acid, distilled water, solution of ammonia, of each as much as may be sufficient. Macerate the opium in 4 pints of distilled water for 30 hours, and bruise it. Afterwards, being digested for 20 hours more, press it; macerate what remains again, and a third time in water, that it may become free from taste, and as often bruise and press it. Evaporate the mixed liquors with a heat of  $140^{\circ}$  to the consistence of syrup; then add 3 pints of distilled water, and when all the dregs have subsided, pour off the supernatant liquor. Gradually add to this 2 ounces of chloride of lead (or as much as may be sufficient) first dissolved in 4 pints of boiling distilled water, till nothing more is precipitated. Pour off the liquor, and wash what remains frequently with distilled water; next, evaporate the liquors mixed together, with a gentle heat as before, that crystals may be formed. Press these in a cloth, then dissolve them in a pint of distilled water, and digest with an ounce and a-half of animal charcoal in a heat of  $120^{\circ}$ , and strain. Lastly, the charcoal being washed, evaporate the liquors cautiously, that pure crystals may be produced. To the liquor poured off from the crystals first separated, a pint of water being previously added to it, gradually pour in, frequently shaking it, as much solution of ammonia as may be sufficient to precipitate all the morphia." In this process, the meconate of morphia of the opium is decomposed by the chloride of lead; meconate of lead is thrown down, and hydrochlorate of morphia retained in the solution, which, having been purified, is decomposed by the addition of the ammonia.

There are many other methods of separating morphia from opium, the details of which are given by Dumas (*Chim. app. aux Arts*, v. 770,) and by Gmelin (*Handbuch*), but the above are those principally resorted to, and more especially Gregory's process, which answers well in the pharmaceutical laboratory, and is adopted in the *Edinburgh Pharmacopœia*.

*Morphia*, when obtained from its alcoholic solution, is in small brilliant and colorless crystals: they are generally six-sided prisms, with dihedral terminations, but their primary form is a right rhombic prism. (BROOKE, *Ann. Phil.*, vi. 118.) When gently heated they become opaque, and lose water: at a higher temperature morphia fuses into a yellow liquid, which becomes white and crystalline on concreting. In the air it burns with a bright resinous flame. Morphia, though apparently nearly insoluble in cold water, has a bitter taste: boiling water dissolves not more than a hundredth of its weight, but the solution is alkaline to delicate tests. It dissolves in 40 parts of cold, and 30 of boiling anhydrous alcohol. It is almost insoluble in ether; hence the method of separating it from narcotine, which is readily soluble in that menstruum. Morphia, according to Wittstock, as quoted by Berzelius, is soluble in potassa and soda; hence the necessity of avoiding the use of those alkalis in its precipitation. Ammonia dissolves it sparingly, so that even that alkali ought not to be used in excess. It forms a soluble compound with lime, upon which Mohr's process above quoted, is founded.

The quantity of morphia obtained from opium is variable; the produce is greatest from Turkey opium, and least from the East Indian and Egyptian. The average is generally estimated at about 1 oz. from the pound.



The determination of the quantity of morphia in any given sample of opium, is a process of some difficulty. It has often been supposed to be in direct ratio to the proportion of meconic acid, but this has been denied by Robiquet (*Journ. de Pharm.*, xxiii. 348), and by Dr. Pereira (*Mat. Med.*, 2d Ed. p. 1742), who thinks that the best method of ascertaining the goodness of opium is the following, suggested by Thiboumèry (*Journ. de Chim. Med.*, 2nd Ser. iv. 405): Prepare an aqueous extract of the opium to be examined, and dissolve it in hot water; add ammonia (not in excess) to the hot liquor, and when cool, filter; wash the precipitate on the filter, first with cold water, then with proof spirit, and afterwards dry it: then boil it with animal charcoal in rectified spirit, and evaporate the filtered liquor, by which the morphia will be obtained. Dr. Pereira suggests the following modification of the process: after the precipitate has been washed and dried, mix it with proof spirit, and add acetic acid drop by drop, until the solution slightly reddens litmus: by this means the morphia, and not the narcotina, will be dissolved, and may be precipitated from the filtered solution by ammonia. Couerbe suggests that the infusion of the sample of opium should be boiled with lime, filtered, and saturated with hydrochloric acid; the morphia may then be precipitated by ammonia. Opium often contains a number of mechanical impurities and adulterations, and not unfrequently pieces of lead and bullets are found in it. Its degree of humidity is also very various, as may be ascertained by drying it upon a water-bath.

Much has been said respecting the methods of detecting morphia by tests: those which are commonly resorted to are *nitric acid*, which, when dropped upon crystallised morphia, forms a bright-red solution; and *neutral perchloride of iron*, which produces a very characteristic blue color (or blue-green), when added to morphia, or to its salts, provided the solutions are not very dilute. *Iodic acid* is, according to Serullas, the best test of the presence of morphia; it produces a reddish-brown color, and the odor of iodine is immediately perceptible. The minutest quantity of morphia has the property of decomposing iodic acid, but in cases where very small quantities are present, it is recommended that a solution of starch should be employed to detect the free iodine. (In reference to the cautions requisite in the detection of opium in cases of medico-legal investigation and evidence, see A. TAYLOR'S *Manual of Med. Jurisp.*, 244.)

Assuming  $C_{35}H_{20}O_6N$ , as the formula of *anhydrous morphia*, and  $C_{35}H_{20}O_6N + 2HO$ , as the formula of *crystallized morphia*, their composition and equivalents will be as follows:

|                        |    |      |     |      |        |       |                                 |     |       |
|------------------------|----|------|-----|------|--------|-------|---------------------------------|-----|-------|
|                        |    |      |     |      |        |       | Liebig,                         |     |       |
| Carbon .....           | 35 | .... | 210 | .... | 71.91  | ....  | 71.80                           |     |       |
| Hydrogen .....         | 20 | .... | 20  | .... | 6.85   | ....  | 6.34                            |     |       |
| Oxygen .....           | 6  | .... | 48  | .... | 16.44  | ....  | 16.90                           |     |       |
| Nitrogen .....         | 1  | .... | 14  | .... | 4.80   | ....  | 4.96                            |     |       |
| <hr/>                  |    |      |     |      |        |       |                                 |     |       |
| Anhydrous morphia..... | 1  |      | 292 |      | 100.00 |       | 100.00                          |     |       |
| <hr/>                  |    |      |     |      |        |       |                                 |     |       |
| Carbon .....           | 35 | .... | 210 | .... | 67.75  | } = { | Morphia....1 .... 292 .... 94.2 |     |       |
| Hydrogen .....         | 22 | .... | 22  | .... | 7.09   |       |                                 |     |       |
| Oxygen .....           | 8  | .... | 64  | .... | 20.65  |       |                                 |     |       |
| Nitrogen.....          | 1  | .... | 14  | .... | 4.51   |       |                                 |     |       |
| <hr/>                  |    |      |     |      |        |       |                                 |     |       |
| Crystallized morphia   | 1  |      | 310 |      | 100.00 |       | 1                               | 310 | 100.0 |

*Salts of Morphia.* These salts are generally obtained by dissolving pure morphia in the dilute acids: they are colorless, and nearly all crystallizable, bitter, and are stated to give a precipitate of morphia with the alkaline carbonates, and with ammonia. They are precipitated by chloride of platinum. Tannine, and infusion of galls, give precipitates with them, which are redissolved by acetic acid.

*Sulphate of Morphia*,  $C_{35}H_{20}O_6N, SO_3 + 6HO$ , crystallizes in groups of acicular crystals, soluble in about twice their weight of water. This salt consists of

|                                  |   |      |     |      |        | Liebig.    |
|----------------------------------|---|------|-----|------|--------|------------|
| Morphia .....                    | 1 | .... | 292 | .... | 75.64  | .... 75.38 |
| Sulphuric acid.....              | 1 | .... | 40  | .... | 10.37  | .... 10.49 |
| Water .....                      | 6 | .... | 54  | .... | 13.99  | .... 14.13 |
| <hr/>                            |   |      |     |      |        |            |
| Crystallized sulphate of morphia | 1 |      | 386 |      | 100.00 | 100.00     |

Dried at  $250^{\circ}$ , this salt loses 5 atoms of water, but retains the remaining atom till heated up to its decomposing point, so that that portion of water seems essential to the constitution of the sulphate.

*Bisulphate of Morphia* is obtained by dissolving the sulphate in excess of acid, and digesting in ether, which removes the excess of free acid, but does not dissolve the bisulphate. (PELLETIER and CAVENTOU.)

*Hydrochlorate of Morphia.*  $C_{35}H_{20}O_6N, HCl$ . This salt is formed in Gregory's process above detailed: it may be produced directly by the action of hydrochloric gas upon morphia; it forms acicular and plumose crystals, soluble in about 20 parts of water, and when the hot solution cools, it concretes into a crystalline mass: this is also the case when the salt is prepared by dissolving morphia in hot liquid hydrochloric acid. Hydrochlorate of morphia is an *anhydrous* salt, composed of

|                               |   |      |     |      |        | Liebig.   |
|-------------------------------|---|------|-----|------|--------|-----------|
| Morphia.....                  | 1 | .... | 292 | .... | 88.75  | .... 88.7 |
| Hydrochloric acid.....        | 1 | .... | 37  | .... | 11.25  | .... 11.3 |
| <hr/>                         |   |      |     |      |        |           |
| Hydrochlorate of morphia .... | 1 |      | 329 |      | 100.00 | 100.0     |

*Nitrate of Morphia* is formed by dissolving morphia in very dilute nitric acid. It yields stellated groups of crystals, soluble in 1.5 of water.

*Phosphate of Morphia* crystallizes in cubes.

*Acetate of Morphia* is frequently formed for medical use by dissolving a given weight of morphia in a sufficient quantity of distilled vinegar. It crystallizes difficultly in acicular bundles. During evaporation, it easily parts with a portion of its acid, and is apt to be of uncertain composition; hence it is less appropriate for medical use than the hydrochlorate or sulphate.

2. CODEIA.  $C_{35}H_{20}O_5N + 2HO$ . This alkaloid was discovered by Robiquet, in 1832, in the hydrochlorate of morphia prepared by Gregory's process. (*Ann. Ch. et Ph.*, li. 259.) On dissolving the mixed hydrochlorates in water, and precipitating the morphia by ammonia, the codeia remains in solution, and crystallizes by subsequent evaporation: it may be also separated by ether. According to Pelletier, 100 pounds of opium yield 6 ounces of codeia; according to Christison, the proportion of codeia varies in the varieties of opium, amounting in Turkey



opium to one-thirtieth, and in East Indian opium to one-twelfth of the hydrochlorate of morphia obtained from those respective varieties.

*Codeia* crystallizes in acicular, or flat prisms, colorless, and transparent. It fuses without decomposition, when heated in a tube to about 300°, and the mass crystallizes on cooling. In the air, it burns away with a smoky flame. Water, at 60°, dissolves 1·26 *per cent.*: at 110°, 3·7, and at 212°, 5·9 *per cent.* When it is present in larger proportions than the boiling water can dissolve, the excess fuses, and remains at the bottom of the solution. Its solution is sensibly alkaline to tests. *Codeia* is soluble in alcohol and in ether, and in the dilute acids, and forms distinct and easily crystallizable salts. Its medicinal action has not been accurately determined. It is distinguished from morphia by its greater solubility in water, and in ether, by its insolubility in fixed alkalis, by its not being reddened by nitric acid, nor blued by perchloride of iron.

The equivalent of *anhydrous codeia* appears to be 284, and its composition

|                        |    |      |     |      |        |           |
|------------------------|----|------|-----|------|--------|-----------|
|                        |    |      |     |      |        | Robiquet. |
| Carbon.....            | 35 | .... | 210 | .... | 73·94  | .... 72·0 |
| Hydrogen .....         | 20 | .... | 20  | .... | 7·05   | .... 7·5  |
| Oxygen .....           | 5  | .... | 40  | .... | 14·08  | .... 15·1 |
| Nitrogen .....         | 1  | .... | 14  | .... | 4·93   | .... 5·4  |
| <hr/>                  |    |      |     |      |        |           |
| Anhydrous codeia ..... | 1  |      | 284 |      | 100·00 | 100·0     |

*Crystallized codeia* includes 2 atoms of water, and its equivalent is 302 (284 + 18). The only salt of *codeia* which has been analyzed, is the *hydrochlorate*; it is anhydrous, and consists of 284 *codeia* + 37 hydrochloric acid, its equivalent being 321.

3. NARCEIA. C<sub>28</sub> H<sub>20</sub> O<sub>12</sub> N. This substance, discovered by Pelletier in 1832, was obtained as follows (*Ann. Ch. et Ph.*, L. 262): An infusion of Turkey opium was filtered and very carefully evaporated till it left a solid extract, which, redissolved in distilled water, left a large portion of crystallised narcotina; this being separated, the liquid was heated to 212°, and a slight excess of ammonia added to throw down morphia, after which the ebullition was continued for 10 minutes to drive off ammonia: on cooling, the morphia crystallized, not pure, but mixed with narcotina and meconia. After having thus separated the greater part of the morphia by ammonia, the residuary liquor was reduced to half its original bulk by evaporation, and on cooling, morphia was again deposited, which being removed, baryta water was added to the liquor, by which meconate of baryta was thrown down and separated by filtration. Subcarbonate of ammonia was then added to the filtered liquor to separate the remaining baryta, and heat applied to drive off the excess of the subcarbonate of ammonia. The liquor was then filtered, evaporated to the consistence of thick syrup, and left for several days in a cool place, when it formed a pulpy mass including crystals: this was suffered to drain, dried by strong pressure in linen, and digested in boiling alcohol; the alcoholic solution, reduced to a small bulk by distillation, furnished on cooling, a crystalline substance: this, purified by repeated solutions and crystallization, is *narceia*.

Pure *narceia* forms white silky crystals, or acicular prisms, inodorous,

bitterish and slightly pungent, soluble in 375 parts of cold, and in 230 of boiling water; soluble in alcohol, but not in ether; fusible at about  $198^{\circ}$ , and concreting into a white translucent and somewhat crystalline mass; it becomes yellow at  $220^{\circ}$ , and at higher temperatures is decomposed: it is more fusible than morphia or narcotina. It is decomposed by the stronger acids, but when diluted, they dissolve and combine with it, producing at first a blue color, which passes into purple or red, and then disappears.

The formula of narceia, derived from Pelletier's analysis, has been assumed as  $C_{32}H_{24}O_{16}N$ ; but the following results of Couerbe are generally regarded as the more exact.

|                   |    |      |     |      |        | Pelletier. |        | Couerbe.   |
|-------------------|----|------|-----|------|--------|------------|--------|------------|
| Carbon .....      | 28 | .... | 168 | .... | 56.37  | ....       | 54.73  | .... 57.02 |
| Hydrogen .....    | 20 | .... | 20  | .... | 6.72   | ....       | 6.52   | .... 6.64  |
| Oxygen .....      | 12 | .... | 96  | .... | 32.22  | ....       | 34.42  | .... 31.58 |
| Nitrogen .....    | 1  | .... | 14  | .... | 4.69   | ....       | 4.33   | .... 4.76  |
| <hr/>             |    |      |     |      |        |            |        |            |
| Anhydrous narceia | 1  |      | 298 |      | 100.00 |            | 100.00 | 100.00     |

4. THEBAIA. PARAMORPHIA.  $C_{25}H_{14}O_3N$ . This crystalline substance, discovered by Thibouméry, and identified by Pelletier (*Ann. Ch. et Ph.*, L. 262), requires, like the former, further examination; it exists in opium in very small proportion, and can only be obtained, therefore, by those who have an opportunity of operating upon large quantities. Thebaia is represented as eminently alkaline, and as forming distinct salts by solution in the dilute acids. It is converted into a resinous product by the stronger acids, and is soluble in alcohol and ether. The formula of thebaia has not been satisfactorily determined. Its crystals lose 2 atoms of water by fusion. Kane represents *anhydrous thebaia* as  $C_{25}H_{14}O_3N$ , and assigns to it the equivalent 202. It has also been analyzed by Couerbe, (*Ann. Ch. et Ph.*, LV. 136.)

|                |    |      |     |      |        | Kane. |        | Couerbe.   |
|----------------|----|------|-----|------|--------|-------|--------|------------|
| Carbon .....   | 25 | .... | 150 | .... | 74.26  | ....  | 74.41  | .... 71.92 |
| Hydrogen ..... | 14 | .... | 14  | .... | 6.93   | ....  | 6.78   | .... 6.38  |
| Oxygen .....   | 3  | .... | 24  | .... | 11.88  | ....  | 11.87  | .... 15.24 |
| Nitrogen ..... | 1  | .... | 14  | .... | 6.93   | ....  | 6.94   | .... 6.46  |
| <hr/>          |    |      |     |      |        |       |        |            |
| Thebaia .....  | 1  |      | 202 |      | 100.00 |       | 100.00 | 100.00     |

5. PSEUDOMORPHIA,  $C_{27}H_{18}O_{14}N$ , is a substance described by Pelletier as occasionally existing in opium; it resembles morphia in many of its properties, but is not poisonous, at least 8 grains produced no effect upon a rabbit; like morphia it is reddened by nitric acid, and strikes a blue color with perchloride of iron; but it does not decompose iodic acid. It appears only to have been analysed by Pelletier, with the following results:

|                     |    |      |     |      |        | Pelletier. |
|---------------------|----|------|-----|------|--------|------------|
| Carbon .....        | 27 | .... | 162 | .... | 52.94  | .... 52.74 |
| Hydrogen .....      | 18 | .... | 18  | .... | 5.88   | .... 5.81  |
| Oxygen .....        | 14 | .... | 112 | .... | 36.60  | .... 37.37 |
| Nitrogen .....      | 1  | .... | 14  | .... | 4.58   | .... 4.08  |
| <hr/>               |    |      |     |      |        |            |
| Pseudomorphia ..... | 1  |      | 306 |      | 100.00 | 100.00     |

6. NARCOTINA.  $C_{48}H_{24}O_{15}N$ . This well-defined and distinct principle was discovered in 1804 by Derosne. (*Ann. de Chim.*, XLV. 257.)



Its peculiarities were first pointed out by Robiquet in 1817. (*Ann. Ch. et Ph.*, v. and li. 275.) Its alkaline characters are not very distinct, but the compounds which it forms with the acids, and its ultimate composition, place it among the alkaloids. It is contained in some kinds of opium, especially in that recently imported under the name of *Egyptian opium*, in a proportion nearly, if not quite, equal to that of the morphia. The effects of this substance upon the animal economy have not been very satisfactorily ascertained, but there can be little doubt that they are perfectly distinct from those of morphia; opium, deprived of narcotina, is supposed to be more directly sedative, and less stimulating; hence the uses of the salts of morphia in preference to opium, and the advantage of using opium, in many instances at least, from which the narcotina has been abstracted. According to Pereira, narcotina is possessed of little activity, and he accounts for the discrepancies respecting its effects, upon the presumption that the first experimenters with it used it in an impure state. Dr. Roots gave gradually increased doses of it, up to a scruple, without injury; the bitterness of its sulphuric solution led him to employ it in intermittents as a substitute for disulphate of quinia; and Dr. O'Shaugnessy has largely and successfully used it in India, as an indigenous substitute for quinia, with great success.

Narcotina appears to exist in opium in a free state; it may be obtained from powdered opium by digesting it in warm ether, which takes up little else than narcotina, and yields it in crystals. When caustic potassa is added to an aqueous solution of opium, so as just to saturate the free acid, the matter which falls consists chiefly of resin and narcotina. When all the soluble parts of opium have been extracted by water, as in making extract of opium, and in the preparation of morphia, the residue, digested in dilute hydrochloric acid, also yields narcotina. Other means of obtaining narcotina and of separating it from morphia, will be evident, from the account of that alkaloid. Dr. Robertson's method consists in boiling the impure morphia in water, and adding sal-ammoniac, as long as ammonia is evolved in consequence of the decomposition of that salt by the morphia, at a boiling heat; the hydrochlorate of morphia so formed is dissolved, and the narcotina remains. According to Liebig, narcotina is best obtained by boiling the residue of opium left in the preparation of morphia, and which has been exhausted by water, in acetic acid, filtering and precipitating by ammonia, which throws down impure narcotina: it may be purified by dissolving it in boiling absolute alcohol with a little animal charcoal, when it crystallizes out of the filtered liquor on cooling.

*Narcotina* is insipid, when pure. It fuses at  $268^{\circ}$ , and when slowly cooled concretes into a crystalline mass. It is deposited from its alcoholic or ethereal solution in well-defined rhombic prisms, insoluble in cold, and very sparingly soluble in hot water; 100 parts of boiling alcohol (sp. gr. 0.825) dissolve about 5 parts of narcotina, 4 of which crystallize on cooling; boiling ether dissolves about 3 or 4 per cent., of which it deposits more than one-half, on cooling. It is soluble in the volatile and fat oils, but insoluble in alkaline solutions and in lime water. It does not render a solution of a persalt of iron blue, nor is it reddened by nitric acid; but sulphuric acid containing a mere trace of nitric acid immediately reddens it. It does not decompose iodic acid. Heated on

paper over a candle it produces a greasy-looking stain. As it does not affect vegetable colors, it is easily recognised from morphia and codeia. It is readily soluble in dilute acids, forming salts which are very bitter, and difficultly obtained in the crystalline state, for when evaporated they are mostly decomposed into acid and narcotina, and crystals of the latter only separate. This is especially the case with the acetate of narcotina, and furnishes a means of separating it from morphia, for the latter substance is retained in permanent combination and solution.

The equivalent of narcotina deduced from its analysis, is 446, its composition being

|                 |    |      |     |      |        | Liebig.    | Pelletier. |
|-----------------|----|------|-----|------|--------|------------|------------|
| Carbon .....    | 48 | .... | 288 | .... | 64.58  | .... 65.27 | .... 65.16 |
| Hydrogen .....  | 24 | .... | 24  | .... | 5.38   | .... 5.32  | .... 5.45  |
| Oxygen .....    | 15 | .... | 120 | .... | 26.90  | .... 25.63 | .... 25.08 |
| Nitrogen .....  | 1  | .... | 14  | .... | 3.14   | .... 3.78  | .... 4.31  |
| <hr/>           |    |      |     |      |        |            |            |
| Narcotina ..... | 1  |      | 446 |      | 100.00 | 100.00     | 100.00     |

*Hydrochlorate of Narcotina* may be obtained in crystals by leaving its concentrated solution to slow evaporation in a warm place, when radiated groups gradually appear, and at length an opaque mass is formed, composed of interwoven needles, which when dried becomes hard and semi-transparent. Better crystals may be obtained by slowly cooling the alcoholic solution of this salt. It produces double salts with the chlorides of mercury, gold, and platinum.

*Sulphate of Narcotina* does not crystallize, but dries on evaporation into a hard mass.

*Acetate of Narcotina* cannot be obtained in a crystalline form; the crystals which are obtained by the evaporation of the acetic solution, being, according to Wittstock, pure narcotina.

*Tannate of Narcotina* is thrown down in curdy flakes on adding tincture of galls to a solution of narcotina.

7. MECONINE.  $C_{10}H_5O_4$ . This substance was discovered by Dublanc and Couerbe. (*Ann. Ch. et Ph.*, xlix. 44: and L. 337.) They obtained it by digesting opium in cold water, filtering the infusion, concentrating it by evaporation, and adding ammonia as long as it occasions a precipitate: after some days the supernatant liquid is poured off, gently evaporated to the consistence of syrup, and left in a cool place for 15 or 20 days, when it deposits granular crystals, which are collected, drained, pressed, and dried by a gentle heat: they contain meconine, narceia, and other substances: they are boiled in alcohol, and the solution is evaporated to about one-third its bulk, when on cooling it deposits crystals, which are collected, dissolved in boiling water, and filtered with animal charcoal: white crystals are obtained of meconine and narceia; ether dissolves the former and leaves the latter; on evaporating the ethereal solution the meconine remains. (This is only an outline of the essential parts of the process: the details of manipulation are omitted, but they will suggest themselves to the practical operator. The quantity of meconine in opium is so small, that from 15 to 20 lbs. must be operated upon satisfactorily to extract it.)

*Meconine* is white, inodorous, slightly acrid on the tongue, soluble in



TABULAR VIEW OF THE PRINCIPAL CHARACTERS OF THE CRYSTALLINE PRINCIPLES OF OPIUM.

| CHARACTERS.                                       | MORPHIA.  | PSEUDO-MORPHIA.  | CODEIA.   | NARCOTINA.   | THEBAIA.  | NARCEA.  | MECONINE.                                     |
|---|---|--|---|--|---|--|---|
| <i>Taste</i> .....                                | Very bitter .....   | .. ? ..  | Bitter .....  | { Insipid; the salts bitter ... }                              | Rather acrid and metallic .....                               | Slightly bitter ..   | Rather acrid.                                 |
| <i>Fusibility</i> .....                           | Fusible .....   | Infusible? .....   | Fusible at 302° ..  | Fusible at 338° ..   | Fusible at 266° ..  | Fusible at 198° ..   | Fusible at 194°.                              |
| <i>Ditto in Boiling Water</i> .....               | Infusible .....   | Infusible .....  | Fusible .....   | .. ..  | .. ..   | Fusible .....  | Fusible.                                      |
| { <i>Cold Water</i> .....                         | { Insoluble, or nearly so .. }                                | Almost insoluble {   | Soluble in 80 pts {   | Insoluble.....   | Very slightly soluble .....                                   | Soluble in 375 pts   | Soluble in 266 pts.                           |
| <i>Boiling Water</i> ..                           | Soluble in 100 pts  | Less soluble {   | Soluble in 17 pts {   | Soluble in 100 parts .....                                     | Soluble in 10 pts   | Soluble in 230 pts   | Soluble in 19 pts.                            |
| <i>Cold Alcohol</i> ....                          | Soluble in 40 pts   | than in {  | Very soluble .. {   | parts .....  | Still more soluble  | Soluble .....  | Soluble.                                      |
| <i>Boiling Alcohol</i> ..                         | Ditto in 30 parts {   | water .. ... {   | Insoluble in the cold ley .....                               | Readily soluble  | Very soluble .....  | More soluble .....   | Soluble.                                      |
| <i>Cold Ether</i> .....                           | Scarcely soluble  | .. ..  | Insoluble in the cold ley .....                               | Insoluble, or nearly so .....                                  | Insoluble, unless the ley be very concentrated ..             | Insoluble .....  | Soluble.                                      |
| { <i>Potash or Soda Ley</i>                       | Soluble .....   | Soluble .....  | Alkaline .....  | Neutral .....  | Alkaline .....  | .. ..  | Soluble.                                      |
| <i>Basic</i> { <i>Action on Test Paper</i> ..     | Alkaline .....  | .. ? ..  | Alkaline .....  | Neutral .....  | Alkaline .....  | Neutral .....  | Neutral                                       |
| <i>quality</i> { <i>Salifiability</i> .....       | Salifiable .....  | Not salifiable .....   | Salifiable .....  | Salifiable .....   | Salifiable? .....   | Not salifiable ..  | Not salifiable.                               |
| <i>Action of Nitric Acid</i> .....                | Reddened; solution red .....                                  | Reddened .....   | Solution not red {  | Made yellow; solution yellow {                                 | Gives it a resinous appearance, and dissolves it {            | Coloured blue by dilute acid .....                             | Solution yellow.                              |
| <i>Coloured blue by Hydroch. Acid</i>             | .. Not ..   | .. Not ..  | .. Not ..   | .. Not ..  | .. Not ..   | Coloured blue ..   | .. Not.                                       |
| <i>Ditto by Sesquichloride of Iron</i> ..         | Coloured blue ..  | Coloured blue ..   | .. Not ..   | .. Not ..  | .. Not ..   | .. Not ..  | .. Not.                                       |
| <i>Coloured blue by Iodine</i> .....              | .. Not ..   | .. ? ..  | .. Not ..   | .. Not ..  | .. Not ..   | Coloured blue ..   | .. Not.                                       |
| <i>Decomposes Iodic Acid</i> .....                | Decomposes Iodic acid .....                                   | .. ? ..  | .. Not ..   | .. Not ..  | .. Not ..   | .. Not ..  | .. Not.                                       |
| <i>Precipitated by Infusion of Nutgalls</i> ..... | Precipitated .....  | .. ? ..  | Precipitated .....  | Precipitated .....   | .. ? ..   | .. ? ..  | .. ?  |
| <i>When fused reddened by Chl. Gas.</i>           | .. Not ..   | .. ? ..  | .. Not ..   | .. Not ..  | .. Not ..   | .. Not ..  | Blood-red.                                    |
| <i>Composition</i> ..                             | C <sub>35</sub> H <sub>20</sub> N <sub>1</sub> O <sub>6</sub> | C <sub>27</sub> H <sub>18</sub> N <sub>1</sub> O <sub>14</sub> | C <sub>35</sub> H <sub>20</sub> N <sub>1</sub> O <sub>5</sub> | C <sub>48</sub> H <sub>24</sub> N <sub>1</sub> O <sub>15</sub> | C <sub>25</sub> H <sub>14</sub> N <sub>1</sub> O <sub>3</sub> | C <sub>23</sub> H <sub>20</sub> N <sub>1</sub> O <sub>12</sub> | C <sub>10</sub> H <sub>5</sub> O <sub>4</sub> |
| <i>Equivalent</i> ..                              | .. 292 ..   | .. 306 ..  | .. 284 ..   | .. 446 ..  | .. 202 ..   | .. 298 ..  | .. 97 (?)                                     |
| <i>Water of Crystallization</i> .....             | 2 atoms .....   | .. ? ..  | 2 atoms .....   | 3 or 4 per cent. ...   | 1 atom .....  | .. ? ..  | None.   |
| <i>Poisonous</i> .....                            | Poisonous .....   | Not poisonous ..   | Poisonous .....   | Inert? .....   | Poisonous .....   | Inert? .....   | Inert?  |

water, alcohol, and ether, and crystallizable; it fuses at  $195^{\circ}$ , and at about  $350^{\circ}$  it distils over unaltered and concretes into a white mass looking like fat. It forms a colorless solution in sulphuric acid diluted with half its weight of water, but on applying heat to this solution it becomes green and is decomposed. When chlorine is passed over fused meconine, it forms a red crystalline compound, and if the chlorine be removed by oxide of silver, a white acid substance is obtained, which Couerbe calls *mechloic acid*, and to which the formula  $C_{14}H_7O_{10}$  has been assigned. With nitric acid meconine yields *nitromeconic acid* =  $C_{20}H_9O_{12}N$ . If meconine be =  $C_{20}H_{10}O_8$ , then nitromeconine may be formed by the substitution of an atom of nitrous acid for 1 atom of hydrogen, and be represented as  $C_{20}\overset{H_9}{NO_4}O_8$ .

The nature of this substance has been hitherto very imperfectly ascertained: according to Couerbe it contains no nitrogen. The formula which best agrees with its analysis is that above given.

The opposite table, showing the distinctive characters of the principal constituents of opium, is inserted by the author's permission, from Dr. Pereira's valuable work on the *Materia Medica*, (vol. ii. p. 1739, 2nd ed.)

8. MECONIC ACID.  $C_{14}H_{11}O_{11}, 3HO = \overline{Mec} + 3HO$ . The existence of a distinct acid in opium was announced by Seguin in 1804 (*Ann. de Ch.*, xcii. 225), and shortly afterwards by Sertuerner, who gave it the above name (from *μηκων*, poppy). (*Ann. de Ch. et Ph.*, v. 21.) It may be most conveniently extracted from the precipitate obtained by adding chloride of calcium to infusion of opium, in the process for procuring morphia (p. 1404). This precipitate is washed first with water, and then with hot alcohol, and mixed with 10 times its weight of water, at  $195^{\circ}$ ; hydrochloric acid is then gradually added, so as to dissolve the *meconate of lime* (which forms the bulk of the precipitate) and leave the sulphate of lime; the solution is filtered, and on cooling deposits crystals of *bimeconate of lime*: these are again dissolved in hot dilute hydrochloric acid, by which the lime is abstracted, and crystals of meconic acid obtained, which, if pure, should leave no residue when burned: they must be redissolved in the acid, and recrystallized, till they are obtained in this state, but care must be taken to keep the temperature of their solutions below  $212^{\circ}$ . To abstract the whole of the coloring matter from this acid, it must be saturated by a weak solution of caustic potassa, and the meconate of potassa dissolved by the aid of gentle heat in a little water: when cold, the fluid part, which retains the color, must be pressed out of the crystals, and these, decomposed as before by hydrochloric acid, ultimately yield the meconic acid in small white crystals, which must be dried at a temperature below  $100^{\circ}$ . (ROBIQUET, *Ann. Ch. et Ph.*, li. 236, liii. 245.)

Meconic acid crystallizes in transparent and micaceous scales of an acid taste, soluble in 4 parts of hot water, and in alcohol. The crystals are permanent in the air, but when heated to  $212^{\circ}$  they lose 21.5 per cent. of water: they then sustain a temperature of  $240^{\circ}$  without decomposition; but if a strong aqueous solution of the acid be boiled, it becomes dark colored, carbonic acid is evolved, and oxalic acid and *comenic* (*metameconic*) acid are formed, together with a brown product. Boiled



in hydrochloric acid meconic acid is resolved into carbonic and comenic acid. If we attempt to whiten meconic acid by animal charcoal, a considerable part of the acid is absorbed and retained by that substance, and can only be again abstracted by the help of a solution of potassa. Meconic acid is decomposed when heated above 250°, evolving carbonic acid, and leaving comenic acid and a little brown matter; at a higher temperature the comenic acid itself is decomposed, and a sublimate of pyromeconic acid is obtained. Meconic acid is difficultly acted on by sulphuric acid, but heated with nitric acid it is rapidly decomposed. When boiled with dilute sulphuric acid it dissolves with effervescence, and crystals of comenic acid separate on cooling. Heated in a solution of potassa meconic acid is decomposed into carbonic and oxalic acid, and a brown matter. A solution of a persalt of iron gives a deep blood-red color to solutions of meconic acid, without occasioning a precipitate. The formula of *anhydrous meconic acid* is C<sub>14</sub> H O<sub>11</sub>, giving the equivalent 173.

|                             |    |       |     |       |        |
|-----------------------------|----|-------|-----|-------|--------|
| Carbon .....                | 14 | ..... | 84  | ..... | 48·55  |
| Hydrogen...                 | 1  | ..... | 1   | ..... | 0·58   |
| Oxygen.....                 | 11 | ..... | 88  | ..... | 50·87  |
| <hr/>                       |    |       |     |       |        |
| Anhydrous meconic acid..... | 1  |       | 173 |       | 100·00 |

The meconic acid dried at 212° is a *tribasic meconate of water* = C<sub>14</sub> H O<sub>11</sub>, 3HO; its equivalent is 200, and its ultimate composition as follows. (LIEBIG, *Ann. Ch. et Ph.*, LXVIII. 6.)

|                            |    |      |     |      |     | Berzelius. | Liebig. |
|----------------------------|----|------|-----|------|-----|------------|---------|
| Carbon .....               | 14 | .... | 84  | .... | 42  | ....       | 42·040  |
| Hydrogen .....             | 4  | .... | 4   | .... | 2   | ....       | 1·995   |
| Oxygen .....               | 14 | .... | 112 | .... | 56  | ....       | 55·965  |
| <hr/>                      |    |      |     |      |     |            |         |
| Meconic acid dried at 212° | 1  |      | 200 |      | 100 |            | 100·000 |
|                            |    |      |     |      |     |            | 100·00  |

The *crystals* of meconic acid have the equivalent 254, and their formula is C<sub>14</sub> H O<sub>11</sub>, 3HO + 6HO. Including therefore their 6 atoms of water of crystallization, they consist of

|                                 |    |       |     |       |        |
|---------------------------------|----|-------|-----|-------|--------|
| Carbon .....                    | 14 | ..... | 84  | ..... | 33·07  |
| Hydrogen .....                  | 10 | ..... | 10  | ..... | 3·94   |
| Oxygen .....                    | 20 | ..... | 160 | ..... | 62·99  |
| <hr/>                           |    |       |     |       |        |
| Crystallized meconic acid ..... | 1  |       | 254 |       | 100·00 |

*Meconates.* In these salts, one, two, or three of the equivalents of water in the hydrated acid, are replaced by one, two, or three equivalents of metallic oxide, so that we have the three following classes of salts; namely,

- 1. MO, 2HO,  $\overline{\text{Mec.}}$
- 2. 2MO, HO  $\overline{\text{Mec.}}$
- 3. 3MO,  $\overline{\text{Mec.}}$

One of the leading characters of this acid and of its salts, is that of forming compounds with the peroxide of iron of an intensely red color, very similar to that of the sulphocyanate of iron; so that the persalts of iron are excellent tests of its presence, and by them opium may sometimes be recognised, where the quantity is so small as to render the morphia very difficult of detection. This red color is destroyed by heat, by sulphurous acid, and by protochloride of tin; but it returns on

exposure to air, or on the addition of a few drops of nitric acid. A few drops of laudanum or other compound of meconic acid in 6 or 8 ounces of distilled water, to which 2 or 3 drops of solution of potassa have been added, is blackened on the addition of a few drops of solution of gold in nitrohydrochloric acid; the effect takes place in a few minutes, when the solutions are even more dilute.

Mr. Cooper, who first suggested this test, uses it as distinctive between meconic acid and sulphocyanic and indigotic acids, all of which redden the persalts of iron, but the former only blackens the potassachloride of gold. All the soluble meconates containing 1 or 2 atoms of fixed base, have an acid reaction, but the soluble tribasic meconates have an alkaline reaction. They are all decomposed by heat, without the production of pyromeconic acid. The monobasic and bibasic meconates of the alkalis and alkaline earths are sparingly soluble in water, but the tribasic salts are more soluble. (LIEBIG.)

*Meconate of Ammonia.* When meconic acid is neutralized by ammonia, two crystalline compounds are obtained, both of which have an acid reaction. When the acid is supersaturated by ammonia, a yellow tribasic meconate is formed.

*Meconate of Potassa.*  $2\text{KO}, \text{HO}, \overline{\text{Mec}}$ . To prepare this salt, the impure meconic acid derived from the salt of lime is heated with water, and a solution of caustic potassa added till it assumes a greenish-yellow color: it then forms a kind of magma which is heated with a little water so as to dissolve it; on cooling, the liquor concretes into a crystalline mass, which after having been pressed between folds of bibulous paper is purified by a second solution and crystallization. This salt forms silky crystals, sparingly soluble in cold water. When hydrate of potassa is added to its solution, a yellow *tribasic meconate* may be obtained,  $3\text{KO}, \overline{\text{Mec}}$ , which when dissolved in a boiling solution of potassa of the density 1.3, concretes, on cooling, into a crystalline mass of oxalate of potassa, containing also carbonate of potassa, and a dark reddish-brown coloring matter. When a little hydrochloric acid is added to a cold saturated solution of the original salt, brilliant needles of the unibasic salt are deposited,  $\text{KO}, 2\text{HO}, \overline{\text{Mec}}$ .

*Meconate of Soda.* There are three of these salts, which closely resemble the corresponding potassa salts.

*Meconate of Lime.*  $\text{CaO}, 2\text{HO}, \overline{\text{Mec}} + 3\text{HO}$ . This salt is procured from an infusion of opium, from which the insoluble alkaloids have been precipitated by soluble bases. For this purpose a solution of chloride of calcium is added to the liquid residue of the preparation of morphia, and after having exactly saturated it by hydrochloric acid, or slightly supersaturated it by acetic acid, it is left to itself, when a brown crystalline precipitate forms in it, composed of meconate of lime, with more or less sulphate of lime, which may be separated by boiling the mixture in 20 parts of water acidulated by hydrochloric acid. On cooling, brown crystals, free from sulphate of lime, are deposited.

A solution of bibasic meconate of potassa occasions no precipitate in a solution of chloride of calcium, but chloride of calcium dropped into a hot saturated solution of the meconate, throws down a white precipitate, soluble in 20 parts of boiling water; and if a little hydrochloric acid be



added to this solution, crystals of the unibasic meconate of lime, having the above formula, are obtained. Saturated with ammonia, the solution of the salt of potassa throws down a gelatinous precipitate from chloride of calcium, which is a *bibasic meconate of lime*,  $2\text{CaO}, \text{HO}, \overline{\text{Mec}} + 2\text{HO}$ .

*Meconate of Baryta*,  $2\text{BaO}, \text{HO}, \overline{\text{Mec}}$ , is sparingly soluble in water, but it dissolves in excess of baryta water, forming a yellow solution. Meconic acid occasions no precipitate in baryta water.

*Meconate of Magnesia*. When carbonate of magnesia is digested in a solution of meconic acid, a difficultly soluble salt is formed; it dissolves in excess of the acid, and yields a salt in brilliant acicular crystals.

*Meconate of Protoxide of Iron*,  $2\text{FeO}, \text{HO}, \overline{\text{Mec}}$ , is a colorless soluble salt, which reddens when exposed to air.

*Meconate of Peroxide of Iron*,  $\text{Fe}_2\text{O}_3, \overline{\text{Mec}}$ , is very soluble, and of a blood-red color. It loses its color by the joint action of light and sulphurous acid, and regains it under the influence of oxidizing agents. Its tint is not affected by chloride of gold, which distinguishes it from the sulphocyanide of iron, which is also red; but is rendered yellow by the salt of gold. Meconic acid does not precipitate persulphate of iron, either in aqueous or in alcoholic solution, but when meconate of ammonia is added to a solution of neutral persulphate of iron, a red precipitate falls, which may be washed with cold water. It is soluble in hot water, and in dilute acids, but not in alcohol. When its aqueous solution is mixed with potassa, ammonia is evolved, and oxide of iron thrown down, and the red color disappears. If hydrochloric acid be then added so as just to saturate the liquor, the red color reappears, but again disappears on adding excess of acid. This salt is a double *meconate of iron and ammonia*. When solutions of meconic acid and of perchloride of iron in pure ether are mixed, a red-brown precipitate falls, which is so soluble as to separate in the form of a red oil-like liquid, if the ether contain any water.

*Meconate of Copper*. Meconic acid throws down a yellow-green, and meconate of ammonia an emerald-green precipitate, when added to a solution of acetate of copper.

*Meconate of Lead*,  $2\text{PbO}, \text{HO}, \overline{\text{Mec}}$ , falls in the form of a white and very difficultly-soluble powder, when a solution of meconic acid is added either to neutral or basic acetate of lead. It is also thrown down by double decomposition, when the corresponding meconate of potassa is mixed with nitrate of lead.

*Meconates of Mercury* may be formed by double decomposition; they form yellow precipitates, insoluble in water. The salt containing the red oxide of mercury is very soluble in a solution of chloride of sodium.

*Meconate of Silver*.  $2\text{AgO}, \text{HO}, \overline{\text{Mec}}$ . When a solution of nitrate of silver is added to a hot saturated solution of meconic acid, a white precipitate falls, insoluble in water. When boiled in water it becomes yellow and is changed into the *tribasic* salt,  $3\text{AgO}, \overline{\text{Mec}}$ , while meconic acid is set free. When the white precipitate is heated, it fuses without deflagrating, and leaves metallic silver. It dissolves in dilute nitric acid and when the solution is boiled, an abundant white precipitate of cyanide

of silver is obtained, the cyanogen being formed by the union of the carbon of the meconic acid with the nitrogen of the nitric acid; oxalic acid is at the same time produced. If great excess of the dilute acid, or if concentrated nitric acid be used, the cyanide is not obtained. When nitrate of silver is added to a solution of meconic acid slightly supersaturated with ammonia, a yellow precipitate falls, which deepens in color when washed and dried, without becoming crystalline; when heated it is decomposed with slight explosion. (LIEBIG. BERZELIUS.)

9. COMENIC ACID.  $C_{12}H_2O_8, 2HO = \overline{Com}, 2HO$ . This acid was discovered by Robiquet, in 1832, who termed it *parameconic acid*. (*Ann. Ch. et Ph.*, li. 254.) Liebig first determined its composition, and gave it the name of *metameconic acid*. (*Ibid.*, liv. 26, and lxviii. 46.) Berzelius afterwards named it *komenic acid*, a term derived by inversion from *mekonic acid*.

When a solution of meconic acid is boiled, it gradually acquires a deep brown color, and evolves carbonic acid; and after some time the liquor deposits hard, colored crystals, of *comenic acid*. They may be rendered colorless by redissolving in boiling water, and treating the liquor with animal charcoal. In this decomposition the meconic acid appears to suffer two distinct changes; one, concerned in the formation of the brown extractive matter, and the other in the production of carbonic and comenic acid. These changes are not necessarily concomitant, but under certain conditions, the one may be induced without the other. Robiquet observed that when hydrochloric acid was added in excess to a boiling solution of meconate of potassa, carbonic acid was evolved with effervescence, and that the liquor deposited crystals of comenic acid, colorless, or nearly so. Liebig found that on boiling meconic acid with hydrochloric acid as long as carbonic acid is evolved, it is entirely converted into comenic acid, a change which Berzelius adduces as an instance of *catalytic action*, in which the *presence* of the hydrochloric acid leads to the resolution of the meconic acid, into comenic and carbonic acid, just as a ferment induces the resolution of sugar into carbonic acid and alcohol, or as platinum resolves peroxide of hydrogen into oxygen and water.

According to Stenhouse, (*Mem. Chem. Soc.*, ii. 117,) comenic acid is best obtained by boiling meconate of lime with great excess of hydrochloric acid; on cooling, hard red crystals of comenic acid are deposited, which are to be dissolved with the aid of heat in a strong solution of carbonate of potassa, so as to saturate it as nearly as possible; the liquor is then filtered whilst boiling hot, and on cooling deposits comenate of potassa, free from lime; the dark-colored mother-liquor is then poured off, the crystals washed with a little cold water, and decomposed by boiling hydrochloric acid, when a crop of crystals of comenic acid is obtained on cooling, which however are still a little colored, and require to be purified by redissolving them in boiling water, treating the solution with animal charcoal, and recrystallizing. This must be repeated till they are quite pure, and burn away when heated upon platinum foil without leaving any residue.

Meconic acid may also be converted into comenic acid by subjecting it to a temperature between  $390^{\circ}$  and  $445^{\circ}$ ; it should not exceed the latter point; carbonic acid is evolved, and comenic acid remains in the



form of a grey and somewhat crystalline powder, which may be purified by crystallization from its hot aqueous solution.

Comenic acid forms hard granular crystals, which require about 16 parts of boiling water for solution, permanent in the air, and sustaining no loss of weight when heated to  $250^{\circ}$  in a stream of dry air. The composition of the comenic acid bears a simple relation to that of the meconic acid. The latter contains 6 atoms of water of crystallization, which it loses when dried at  $250^{\circ}$ , together with 3 atoms of basic water, which may be replaced by metallic oxides, and a part of which may also be expelled by heating it *above*  $250^{\circ}$ , when the elements of 2 atoms of carbonic acid are also given off. 1 atom of meconic acid dried at  $250^{\circ}$ , contains the elements of 1 atom of anhydrous comenic acid, 2 atoms of water, and 2 atoms of carbonic acid.

|                              |  |
|------------------------------|--|
| 1 atom of comenic acid ..... | C <sub>12</sub> H <sub>2</sub> O <sub>8</sub>  |
| 2 „ water .....              | H <sub>2</sub> O <sub>2</sub>                  |
| 2 „ carbonic acid.....       | C <sub>2</sub> O <sub>4</sub>                  |
| <hr/>                        |  |
| = 1 „ meconic acid .....     | C <sub>14</sub> H <sub>4</sub> O <sub>14</sub> |

The equivalent of the *anhydrous comenic acid* is 138, and that of the *crystallized acid* 156, their composition being

|  |    |       |     |       |        |
|--|----|-------|-----|-------|--------|
| Carbon .....   | 12 | ..... | 72  | ..... | 52.17  |
| Hydrogen .....   | 2  | ..... | 2   | ..... | 1.45   |
| Oxygen.....  | 8  | ..... | 64  | ..... | 46.38  |
| <hr/>  |    |       |     |       |        |
| Anhydrous comenic acid.....  | 1  |       | 138 |       | 100.00 |
| <hr/>  |    |       |     |       |        |
| Carbon .....   | 12 | ...   | 72  | ...   | 46.15  |
| Hydrogen .....   | 4  | ...   | 4   | ...   | 2.56   |
| Oxygen .....   | 10 | ...   | 80  | ...   | 51.29  |
| <hr/>  |    |       |     |       |        |
| Crystallized comenic acid  | 1  |       | 156 |       | 100.00 |
| <hr/>  |    |       |     |       |        |
| $\left. \begin{array}{l} \text{Anhydrous acid } 1 \dots 138 \dots 88.46 \\ \text{Water} \dots\dots\dots 2 \dots 18 \dots 11.54 \end{array} \right\} =$ |    |       |     |       |        |
| <hr/>  |    |       |     |       |        |
| Crystallized comenic acid  | 1  |       | 156 |       | 100.00 |
| <hr/>  |    |       |     |       |        |

*Comenates.* These salts have been imperfectly examined. Comenic acid acquires a yellow color by excess of alkali; so that the alkaline and earthy comenates are best prepared, according to Berzelius, by adding the acid to an excess of the acetic salt of the base, evaporating to dryness in a water-bath, and dissolving out the excess of the acetate, by means of alcohol, which leaves the comenate undissolved; it may then be dissolved in water and crystallised. The comenates are reddened like the meconates by the persalts of iron, but when they are decomposed by hydrochloric acid in the cold, and the evolved acid crystallised from its hot aqueous solution, the nature of the acid is easily determined.

*Comenate of Ammonia.* When a neutral solution of this salt is evaporated, it yields an aggregate of small prismatic crystals of acid comenate =  $\text{NH}_4 \text{O}, \text{HO}, \overline{\text{Com}}$ .

*Comenate of Potassa,*  $2\text{KO}, \overline{\text{Com}}$ , is difficultly soluble in cold water: its hot solution deposits it in mamillary crystals.

*Comenate of Peroxide of Iron.* When persulphate of iron is added to a cold and somewhat concentrated solution of comenic acid, the liquor assumes a deep blood-red color; after standing for some hours it grows paler, and slowly deposits a quantity of small shining jet black crystals. Stenhouse observes that this salt is generally described as very soluble,

a mistake which has probably arisen from the black powder being so unlike a salt as to have been overlooked. The crystals are hard, gritty, and almost tasteless, and difficultly soluble in cold and hot water. When washed with cold water, it runs off nearly colorless, but if kept standing over them, it becomes pink; the solution in boiling water is pale red; their powder is dark brown. They contain 18.6 *per cent.* of peroxide of iron, and consist, according to Stenhouse, when dried at  $212^{\circ}$ , of  $C_{24}H_{11}O_{23} + Fe_2O_3$ . Comenate of ammonia, mixed with persulphate of iron, also yields this salt; but if comenate of ammonia be added to a hot instead of a cold solution of persulphate of iron, and the mixture kept for some hours at  $150^{\circ}$ , none of the black crystals are deposited, and the red color of the liquid disappears, and it becomes yellow. In this case, tests show that the peroxide of iron has been reduced to the state of protoxide, and the red color reappears on the addition of more of the persulphate, or of a little nitric acid.

*Comenate of Copper.* When a solution of sulphate of copper is mixed with a boiling solution of comenic acid, the mixture acquires a green color, and green microscopic crystals are deposited. Comenate of potassa throws down a flocculent precipitate of the same salt. Comenic acid produces scarcely any precipitate in acetate of copper, but when the mixed solutions are evaporated the comenate is deposited.

*Comenate of Lead.* Acetate of lead dropped into a solution of comenic acid, produces a white granular precipitate, which easily redissolves till the greater part of the acid has combined with oxide of lead; the precipitate then acquires a yellow tinge. Dried at  $212^{\circ}$ , this comenate retains an atom of water, being  $2PbO, \overline{Com}, HO$ . The mixture of an alkaline comenate with a soluble salt of lead gives the same compound.

*Comenate of Silver,*  $2AgO, \overline{Com}$ , is thrown down in the form of a yellow powder on adding an alkaline comenate to nitrate of silver. When a hot saturated solution of comenic acid is mixed with a solution of nitrate of silver, the resulting precipitate is an *acid comenate*,  $= AgO, HO, \overline{Com}$ .

10. PYROCOMENIC ACID.  $C_{10}H_3O_5, HO$ . Sertuerner, who first obtained this acid, regarded it as meconic acid; Pelletier first pointed out the error, and in 1832 (*Ann. Ch. et Ph.*, li. 251), examined and analysed it, and gave it the name of *pyromeconic acid*. But, as Berzelius observes (*Lehrbuch*, iv. 280), inasmuch as it is not produced from meconic acid, except it has undergone the intermediate change into comenic acid, the term *pyrocomenic acid* is most appropriate.

According to Stenhouse (*Mem. Chem. Soc.*, ii. 1), who has more recently studied this acid, it is best obtained by maintaining either meconic or comenic acid at a temperature between  $510^{\circ}$  and  $550^{\circ}$ , in a retort: pyrocomenic acid then passes into the receiver, partly as an oily liquid, and partly as a crystalline sublimate. Towards the close of the distillation, a few crystals of paracomenic acid appear on the sides and neck of the retort. The first product of pyrocomenic acid is very impure, being contaminated by empyreumatic oil and acetic acid; it may be freed from these by pressing it between folds of blotting-paper, and cautiously redistilling it at a comparatively low temperature; it is then





with hydrated lime, and filtering the warm liquor; on cooling, it deposits the salt in small hard crystals.

*Pyrocomenate of Iron.* When freshly precipitated peroxide of iron is boiled in a solution of pyrocomenic acid, it forms a brownish-red compound, insoluble in water; but when a few drops of hydrochloric acid are added, it dissolves with a fine red color, and is deposited, on cooling, in cinnabar-red crystals. The best way of obtaining this salt in distinct crystals is to add persulphate of iron to a tolerably dilute boiling solution of pyrocomenic acid, and allow it to cool very slowly; they are deposited, after some hours, in distinct rhomboids, much resembling garnets; they are hard, brittle, very difficultly-soluble either in hot or cold water, and their solution is of a reddish-yellow color. According to Stenhouse's analysis, these crystals are anhydrous, and are  $= \text{Fe O}_3, 3[\text{C}_{10} \text{H}_3 \text{O}_5]$ .

*Pyrocomenate of Copper.* When excess of hydrated oxide of copper is boiled with pyrocomenic acid, the liquor assumes a bright green color, and when filtered, an emerald-green salt is deposited on cooling; it crystallizes in long slender brittle needles, very slightly soluble in cold water and alcohol, and but sparingly soluble in hot water. When dried *in vacuo*, and then kept for some time at  $212^\circ$ , they lose no weight. They are anhydrous, and have the formula  $\text{CuO}, \text{C}_{10} \text{H}_3 \text{O}_5$ . (STENHOUSE.)

*Pyrocomenate of Lead.* This salt is formed by adding hydrated oxide of lead to a hot solution of pyrocomenic acid; when nearly saturated, the lead-salt falls. It consists of  $\text{PbO}, \text{C}_{10} \text{H}_3 \text{O}_5$ . (ROBIQUET.)

*Pyrocomenate of Silver.* When oxide of silver is added to a cold solution of pyrocomenic acid, it immediately forms a bulky greyish compound, which is but slightly soluble and has very little permanence, quickly decomposing, even in the cold, and becoming black. If boiled in a glass tube, its inner surface becomes coated with a mirror of metallic silver, the oxide being reduced without the evolution of any gas. When pyrocomenic acid is added to a solution of nitrate of silver, no precipitate or change of color takes place, and it requires to be boiled for some time before even a partial reduction ensues; but if a few drops of ammonia are first added to the nitrate, the pyrocomenic acid immediately produces a bright yellow gelatinous precipitate, soluble both in water and in alcohol; it quickly changes color, even *in vacuo*, and becomes dark brown. It deflagrates slightly when strongly heated. It contains about 52 per cent. of oxide of silver. (STENHOUSE.)

11. PARACOMENIC ACID. It has been above stated that in the process for obtaining pyrocomenic acid, some crystals of paracomenic acid are produced towards the end of the operation. This acid was first noticed by Gruner and Robiquet. Stenhouse obtained it by heating meconic acid in Mohr's subliming apparatus (see *Benzoic Acid*, p. 1356), to as high a temperature as the paper diaphragm will admit of without charring; the greater portion of the pyromeconic (pyrocomenic) acid produced at the same time was either destroyed or dissipated, and but little of it found with the crystals of the *paracomenic* acid, in the cap and on the diaphragm. The latter acid is separated by washing the crystals in cold water or alcohol, in both of which it is scarcely soluble, while the pyrocomenic acid is, on the other hand, easily washed away.



When first sublimed, paracomenic acid is yellow, but by dissolving it in boiling water, and digesting with animal charcoal, the filtered liquor deposits it on cooling in hard crystalline grains, only slightly yellow, and giving a white powder. If these crystals be not quickly dried, they become pale red, and their solutions, though reddish while cold, become nearly colorless when heated: in appearance, solubility, and acid reaction, they much resemble comenic acid, with which they are *isomeric*, having the formula  $C_{12}H_4O_{10}$ , but they are distinguished by the following reactions: (1.) Paracomenic acid produces no precipitate in a solution of acetate of copper, while comenic acid causes a copious yellowish-green precipitate. (2.) When added to neutral acetate of lead, paracomenic acid throws down a small quantity of a white granular precipitate, which instantly disappears if the liquor is stirred, being apparently dissolved in the free acetic acid present, for it reappears and remains permanent, on the addition of a few drops of ammonia. Comenic acid, on the contrary, causes a bulky yellowish precipitate in acetate of lead, not soluble even in great excess of acetic acid. Neither of the acids precipitate salts of lime, baryta, or strontia, nor do they produce any change in solutions of corrosive sublimate or of chloride of platinum. They agree in giving a pale red color to a solution of emetic tartar, but cause no precipitate. Paracomenic acid also closely resembles comenic acid, in its silver salts, of which it appears to form two: when its solution is added to nitrate of silver, it occasions a copious white granular precipitate; and when the acid has been previously neutralised with ammonia it gives with nitrate of silver, a yellow gelatinous precipitate. Both acids give a similar red color with the persalts of iron, and on standing, the liquor yields a deposit of the small black crystals above described. (STENHOUSE.)

12. OPIANIC ACID. This acid was discovered by Wöhler and Liebig (*Chim. Organ.*, ii. 602,) and has been especially studied by the former chemist. It is obtained by dissolving narcotina in great excess of dilute sulphuric acid, heating the solution to its boiling-point, and then adding finely-pulverized binocide of manganese in small successive portions; carbonic acid is evolved, and the liquor acquires a yellow color. When excess of the oxide has been added, so that gas is no longer evolved, the mixture is boiled for a short time, there being also excess of sulphuric acid, and it is then filtered whilst boiling hot. The yellow filtered liquor deposits on cooling acicular crystals of opianic acid, which when washed, drained, and pressed in bibulous paper, may be redissolved in water, and treated by a solution of hypochlorite of soda for the purpose of decoloration. The solution is then heated to its boiling-point, and having added to it excess of hydrochloric acid, and filtered whilst hot, it deposits colorless crystals of opianic acid. When the mother-liquor is again boiled with a little sulphuric acid and binocide of manganese, it often yields a second crop of opianic acid, especially if too little sulphuric acid had been used in the first instance.

Opianic acid forms small lamellar, or reticulated and arborescent crystals of a slightly bitter and acid taste, fusible at  $285^{\circ}$  without loss of weight. Heated in the air, it exhales a balsamic odor, and burns with a bright smoky flame. It is very sparingly soluble in cold water, but dissolves so abundantly in boiling water, that the solution concretes on

cooling. The probable formula of this acid, in its hydrated or crystalline form, is, according to the analysis of Wöhler,  $C_{20}H_8O_9 + HO$ . But Berzelius justly observes that a formula more consistent with the experimental results is, for the *hydrated acid*,  $C_{20}H_{10}O_{10}$ , or  $C_{20}H_9O_9 + HO$ , as the following analyses show.

|                                |    |      |     |      |        |      |                   |
|--------------------------------|----|------|-----|------|--------|------|-------------------|
| Carbon .....                   | 20 | .... | 120 | .... | 57.14  | .... | Wöhler.<br>57.474 |
| Hydrogen.....                  | 10 | .... | 10  | .... | 4.76   | .... | 4.990             |
| Oxygen.....                    | 10 | .... | 80  | .... | 38.10  | .... | 37.536            |
| <hr/>                          |    |      |     |      |        |      |                   |
| Crystallized opianic acid .... | 1  |      | 210 |      | 100.00 |      | 100.000           |

The elements of *opianate of silver* were found to be

|                               |    |      |     |      |        |      |        |
|-------------------------------|----|------|-----|------|--------|------|--------|
| Carbon .....                  | 20 | .... | 120 | .... | 37.86  | .... | 37.85  |
| Hydrogen .....                | 9  | .... | 9   | .... | 2.84   | .... | 3.10   |
| Oxygen .....                  | 9  | .... | 72  | .... | 22.71  | .... | 22.36  |
| Oxide of silver .....         | 1  | ..   | 116 | .... | 36.59  | .... | 36.69  |
| <hr/>                         |    |      |     |      |        |      |        |
| Opianate of silver (dry) .... | 1  |      | 317 |      | 100.00 |      | 100.00 |

The ultimate composition, therefore, of the *anhydrous opianic acid* will be

|                            |    |       |     |       |        |
|----------------------------|----|-------|-----|-------|--------|
| Carbon .....               | 20 | ..... | 120 | ..... | 59.70  |
| Hydrogen .....             | 9  | ..... | 9   | ..... | 4.47   |
| Oxygen .....               | 9  | ..... | 72  | ..... | 35.93  |
| <hr/>                      |    |       |     |       |        |
| Anhydrous opianic acid.... | 1  |       | 201 |       | 100.00 |

Opianic acid fused in chlorine produces hydrochloric acid, and a brown uncrystallized compound which contains chlorine, is easily fusible, and has the odor of myrrh. When sulphurous acid is passed through a solution of opianic acid in hot water, the liquor acquires a peculiar bitter and sweet taste, and when gently evaporated, leaves a transparent inodorous crystalline mass. When this is acted on by water, it becomes milk-white, and smells of sulphurous acid; opianic acid separates, and *opianosulphurous acid* and sulphurous acid are held in solution. If this solution be saturated by carbonate of baryta or carbonate of lead, an insoluble sulphite of baryta or of lead separates, and an *opianosulphite* of those bases remains in solution, and may be obtained in well-defined hydrated crystals on evaporation. Wöhler has analyzed these salts, and if MO represent the base, they are constituted according to the formula,  $MO, C_{20}H_7O_7, 2SO_2$ ; so that in these salts 2 equivalents of the hydrogen of the acid are in fact replaced by 2 equivalents of sulphur; or 2 equivalents of *water*, by 2 of sulphurous acid.

When sulphuretted hydrogen is passed into a boiling solution of opianic acid, it has no apparent effect till the temperature falls to  $160^\circ$ , when it becomes turbid, and deposits a substance having the appearance of sulphur, but which is *sulphopianic acid*. Many hours are required for the entire precipitation of this compound, and if, when the whole has been thrown down, the supernatant liquor be heated to its boiling-point, the precipitate fuses into an oil-like liquid, which on cooling concretes into a transparent amorphous yellow substance. It softens below  $212^\circ$ , but at that temperature it is perfectly fluid; at a higher temperature it begins to be decomposed, and forms a yellow vapor, which condenses in acicular crystals, insoluble in water, but soluble in alcohol.



*Sulphopianic acid* is inflammable, and forms a yellow solution in alcohol. The formula assigned to this acid, by Berzelius, is  $C_{20}H_{10}O_8S_2$ ; he represents its rational formula as  $HO, + C_{20}H_7O_7, 2HS$ .

When a solution of *sulphopianate of ammonia* is mixed with nitrate of silver, a brown precipitate is thrown down, which, if left in the liquor, speedily blackens, but which may be preserved if immediately collected upon a filter, and dried *in vacuo*. It may be fused, even upon paper, without losing weight, but at higher temperatures it exhales fumes like the acid, and leaves sulphuret of silver. With acetate of lead a similar precipitate is produced, which speedily blackens, and if boiled in the fluid, is converted into sulphuret of lead.

In reference to the facility with which, in the case of opianic acid, 2 atoms of water are replaced by 2 atoms of sulphurous acid, or 2 atoms of sulphuretted hydrogen, Wöhler has suggested that that acid may possibly be a *coupled acid*, the real acid base of which is a substance  $= C_{20}H_7O_7$ , and which is combined in opianic acid with 2 atoms of water; in opianosulphurous acid, with 2 atoms of sulphurous acid; and in sulphopianic acid, with 2 atoms of sulphuretted hydrogen.

*Hemipinic Acid*. When peroxide of lead is added to a saturated boiling solution of opianic acid, and sulphuric acid dropped into the mixture till carbonic acid begins to be evolved, a salt of lead is found in the cooled liquor, from which, by the further careful addition of sulphuric acid, the oxide of lead may be separated in the form of sulphate of lead; the liquor is then filtered, evaporated, and set aside, when crystals are obtained, which, if blended with any unchanged opianic acid, must be redissolved in a little hot water and recrystallized, so as to separate it. The substance thus obtained has been called by Wöhler *Hemipinic* (semiopianic?) *acid*. It forms colorless and transparent four-sided prisms of a slightly sour and astringent taste; dried at  $212^\circ$ , they effloresce, and lose water of crystallization. The dried acid fuses at  $356^\circ$ , and concretes on cooling, and when heated between two capsules, may be sublimed like benzoic acid. It is inflammable, burning with a smoky flame. It is difficultly soluble in cold water, and the solution has a strong acid reaction; it is very soluble in alcohol. Boiled with peroxide of manganese and dilute sulphuric acid, it is entirely resolved into carbonic acid and water. In its *crystallized* state its formula is  $C_{10}H_6O_7$ ; the formula of the acid dried at  $212^\circ$  is  $C_{10}H_5O_6$ , and that of the *anhydrous acid*, as it exists in combination with bases, is  $C_{10}H_4O_5$ .

|                               |    |      |     |      |        | Berzelius.  |
|-------------------------------|----|------|-----|------|--------|-------------|
| Carbon .....                  | 10 | .... | 60  | .... | 57.69  | .... 57.735 |
| Hydrogen .....                | 4  | .... | 4   | .... | 3.84   | .... 3.837  |
| Oxygen .....                  | 5  | .... | 40  | .... | 38.47  | .... 38.428 |
| <hr/>                         |    |      |     |      |        |             |
| Anhydrous hemipinic acid .... | 1  |      | 104 |      | 100.00 | 100.000     |

In its conversion into hemipinic acid the opianic acid loses 1 atom of hydrogen, and acquires 1 atom of oxygen,  $C_{20}H_9O_9$ , becoming  $2[C_{10}H_4O_5]$ .

The salts of the hemipinic acid have been very imperfectly examined. *Hemipinate of ammonia*,  $NH_4O, C_{10}H_4O_5$ , is crystallizable, permanent in the air, and very soluble. *Hemipinate of lead* and *hemipinate of silver*

form white insoluble precipitates. The lead-salt is soluble in solution of acetate of lead, from which it crystallizes in tufts.

*Opiummon.* When a solution of opianate of ammonia is evaporated to dryness, and the residue acted on by water, it is only partially dissolved, and a white substance remains, which is *opiammon*. The salt is entirely changed into this product if heated, under constant stirring, to a temperature somewhat above  $212^{\circ}$ , till it no longer gives off ammonia.

Opiummon is a pale-yellow powder, appearing crystalline under a powerful magnifier, easily fusible, and giving off a yellow aromatic vapor when highly heated; it is insoluble in cold water, and very sparingly in boiling water, giving a yellow acid solution. Boiling alcohol dissolves it somewhat more copiously, and the solution deposits it, together with some opianic acid, on cooling. Cold sulphuric acid forms with it an orange-colored solution, which becomes milky when diluted, but again transparent if heated, and it then deposits opianic acid, as it cools, and retains an ammoniacal salt in solution. It dissolves in caustic ammonia, yielding opianate of ammonia. Its formula is  $C_{40}H_{19}O_{16}N$ .

|                |    |      |     |      |        | Wöhler.    |
|----------------|----|------|-----|------|--------|------------|
| Carbon .....   | 40 | .... | 240 | .... | 59.85  | .... 59.80 |
| Hydrogen ..... | 19 | .... | 19  | .... | 4.73   | .... 4.82  |
| Oxygen .....   | 16 | .... | 128 | .... | 31.92  | .... 31.62 |
| Nitrogen ..... | 1  | .... | 14  | .... | 3.50   | .... 3.76  |
| <hr/>          |    |      |     |      |        |            |
| Opiummon.....  | 1  |      | 401 |      | 100.00 | 100.00     |

This compound may be regarded, therefore, as containing the elements of 1 atom of ammonia, 2 of water, and 2 of opianic acid, or as  $NH_4O, HO, 2[C_{20}H_7O_7]$ . Or it may be considered as an opianic imide (opianimidic acid)  $= NH, + C_{20}H_9O_7 + C_{20}H_9O_9$ ; or as  $NH + 2[C_{20}H_9O_8]$ .

When opiammon is added to a solution of caustic potassa, the liquor soon assumes a yellow color, and evolves ammonia; the same result is obtained with a carbonated alkali. If the yellow liquor be then boiled till it ceases to evolve ammonia, it holds, together with opianic acid, a new acid in combination, which Wöhler has termed *Xanthopenic acid*, and which is precipitated in yellow flocks on adding excess of hydrochloric acid to the hot liquor. Separated upon a filter and dried, this substance forms a lemon-yellow powder, fusible, and very soluble in potassa. It contains nitrogen, but has not been further examined.

13. COTARNINA.  $C_{25}H_{13}O_6N + 2HO$ . This is an artificial organic base, formed along with opianic acid in the above-described decomposition of narcotina. The reddish-yellow liquid from which the opianic acid has subsided is treated with chloride of platinum, when a platinumchloride of cotarnina is obtained, which Wöhler decomposed by sulphuretted hydrogen, and so obtained a hydrochlorate of cotarnina. Blyth obtained this compound as follows. (*Mem. Chem. Soc.*, II., 168.) A solution of narcotina in dilute hydrochloric acid was precipitated by bichloride of platinum, and the precipitate formed into a thin paste by the addition of distilled water; a large excess of bichloride of platinum (fully equal to that used for the precipitation) was then added, and the whole heated in a basin. When it became warm, the color changed from yellow to



orange, and traces of opianic acid were formed; the fluid then became darker-colored, the platinum double salt fused, and a quantity of opianic acid made its appearance. The ebullition was then continued, when the opianic acid was redissolved, and the surface of the liquid became covered with dark-red crystals: these were separated by rapid filtration, and washed with hot water, when acicular crystals of opianic acid were deposited on cooling. The mother-liquor was then decanted and evaporated, when a further portion of opianic acid was obtained, but it was now mingled with long crystals of a rhombic prismatic form.

The dark-red crystals are a *platinochloride of cotarnina*, from which the base may be separated, by boiling them in a solution of ammonia, and passing sulphuretted hydrogen through the hot liquor. The mixture was then evaporated to dryness on a water-bath, and the residue treated with distilled water, to which hydrochloric acid was added, till the reaction was feebly acid, in order to decompose the soluble double salt of bisulphuret of platinum and ammonium formed during the reduction of the platinochloride of cotarnina. On filtering, a fluid passed through of a dark-brown color, from which, on the addition of caustic potassa, the cotarnina was precipitated. The whole precipitate was redissolved in hydrochloric acid, boiled with animal charcoal, filtered, and again thrown down by potassa.

Pure cotarnina forms stellated groups of colorless needles. It fuses at  $212^{\circ}$ , losing 7 per cent. of its weight. It is slightly soluble in cold, but more so in hot water. With alcohol it forms a brown solution, from which crystallized cotarnina cannot again be obtained. It is readily soluble in ether and in ammonia, but not in potassa. With nitric acid it forms a red solution. The persalts of iron do not affect its color. Its watery solution precipitates salts of copper, and of protoxide of iron. Its salts are very soluble.

The elements of *crystallized cotarnina* are

|                              |    |      |     |      |        | Blyth.     |
|------------------------------|----|------|-----|------|--------|------------|
| Carbon .....                 | 25 | .... | 150 | .... | 61.73  | .... 61.41 |
| Hydrogen .....               | 15 | .... | 15  | .... | 6.17   | .... 6.38  |
| Oxygen .....                 | 8  | .... | 64  | .... | 26.33  | .... 26.69 |
| Nitrogen .....               | 1  | .... | 14  | .... | 5.77   | .... 5.52  |
| <hr/>                        |    |      |     |      |        |            |
| Crystallized cotarnina ..... | 1  |      | 243 |      | 100.00 | 100.00     |

The equivalent of *anhydrous cotarnina*,  $= \text{C}_{25} \text{H}_{13} \text{O}_6 \text{N}$ , is 225. *Hydrochlorate of cotarnina* forms long silky crystals, very soluble, and giving double salts with the chlorides of mercury and of gold: its formula is  $\text{C}_{25} \text{H}_{13} \text{O}_6 \text{N}, \text{HCl}, + 5\text{HO}$ .

Besides the bodies already mentioned, the oxidation of narcotina produces another basic substance, which Dr. Blyth has termed *Narcogenine*,  $= \text{C}_{36} \text{H}_{19} \text{O}_{10} \text{N}$ ; he regards it as intermediate between narcotina and cotarnina. It forms a crystallizable double salt with chloride of platinum, but when separated, it is resolved into the two preceding bases, with the formation of carbonic acid; 2 equivalents of narcogenine,  $2[\text{C}_{36} \text{H}_{19} \text{O}_{10} \text{N}]$  with 2 of oxygen, containing the elements of 1 equivalent of narcotina, 1 of cotarnina, and 1 of carbonic acid.

## II. CINCHONIA. QUINIA. ARICINA. CINCHONIC ACID.

The existence of a peculiar principle in *pale Peruvian bark*, (the bark of the *Cinchona Condaminea* or *lancifolia*,) was originally suggested by the late Dr. Duncan; he considered it as the source of its medicinal powers, and proposed to call it *Cinchonine*; it was afterwards procured in a crystalline form by Dr. Gomès, of Lisbon; but its peculiar alkaloid properties, and ready and certain methods of preparing it, were first made known by Pelletier and Caventou, in 1820. (*Ann. Ch. et Ph.*, xv. 291 and 337.) They also discovered another analogous but distinct principle in *Yellow Peruvian Bark* (*Cinchona cordifolia*), which has been termed *Quinia*; and in the *Red Peruvian Bark* (*Cinchona oblongifolia*), they found the two preceding alkaloids, nearly in equal proportions. In 1829, Pelletier and Coriol discovered a third alkaloid in a species of bark from Arica, the botanical history of which is not known, but which they have termed *Aricina*.

1. CINCHONIA. *Cinchonine*.  $C_{20}H_{12}ON = \overset{+}{\text{Cin}}$ . This alkaloid may be obtained from the principal varieties of pale or gray Peruvian bark, (*Cinchonæ pallidæ*. PEREIRA. *Quinquinas gris*. GUIBOURT.) The *Cinchona rubiginosa*, *Condaminea*, and *Huanuco* or *cinerea*, especially the latter, have been chiefly employed. A pound of the bruised bark (*Cinchona lancifolia* of the Pharmacopœia) is boiled in about a gallon of water, acidulated by 3 fluid drachms of sulphuric acid. A similar decoction is repeated with about half the quantity of liquid, and so on, till all the soluble matter is extracted. The decoctions are then mixed and strained, and powdered lime added, in a proportion somewhat greater than necessary to saturate the acid: the precipitate that ensues (a mixture chiefly of cinchonia and sulphate of lime) is collected, *carefully* dried, and boiled for some minutes in strong alcohol, which is then decanted off, while hot, and fresh portions are successively added for the repetition of the same operation, until it ceases to act upon the residue, which is now little else than sulphate of lime. The different alcoholic solutions are then put into a retort or still, and considerably evaporated; during which, and especially on cooling, cinchonia is deposited. When the whole is thus collected, the cinchonia must be redissolved in alcohol, and crystallized by slow evaporation. It may be deprived of color and slight impurities by the action of animal charcoal, and two or more crystallizations. In the preceding process hydrochloric acid may be used instead of sulphuric, in which case the precipitate is not encumbered with sulphate of lime.

Pelletier and Caventou obtained cinchonia by digesting 1 part of the bruised bark in 3 of alcohol; this was repeated three times in order to exhaust the bark; the alcoholic tinctures were then mixed with a little water, and the alcohol distilled off. The turbid residue poured upon a filter left a reddish substance, which was washed with water slightly alkalisied by potassa till the liquor passed colorless. The matter now remaining on the filter was impure cinchonia. It was purified by dissolving it in very weak hydrochloric acid; a little magnesia was then added to the solution, which was gently heated, and a precipitate obtained consisting of cinchonia mixed with the excess of magnesia.



When cold, this precipitate was separated upon a filter and washed with water till it passed through colorless. The precipitate was then dried, and dissolved in boiling alcohol, which on cooling deposited crystals of cinchonia, requiring to be purified, either by washing them with cold ether, or by redissolving in alcohol and recrystallizing.

*Cinchonia* is thus obtained in the form of white semitransparent crystals, requiring about 2500 parts of water, at 212°, for their solution, and are almost insoluble in cold water. They have little taste, but become intensely bitter upon the addition of almost any acid. They restore the blue color of reddened litmus. They are sparingly soluble in cold alcohol, ether, and fixed oils; but more abundantly soluble in boiling alcohol, and the solution deposits crystals on cooling, and becomes milky when dropped into water.

When cinchonia is carefully heated, a portion of it appears to sublime in brilliant acicular crystals, but there is always more or less decomposition attending the process, and if it be suddenly and highly heated in a small tube retort, ammonia, hydrocyanic acid, and a peculiar oily matter, smelling like naphtha, are among the products, and a bulky carbon remains. The equivalent of cinchonia is 154, its elements being

|                 |    |      |     |      |       | Dumas and<br>Pelletier. |        | Liebig.    |
|-----------------|----|------|-----|------|-------|-------------------------|--------|------------|
| Carbon.....     | 20 | .... | 120 | .... | 78.4  | ....                    | 78.67  | .... 78.18 |
| Hydrogen .....  | 12 | .... | 12  | .... | 7.2   | ....                    | 7.06   | .... 7.66  |
| Oxygen .....    | 1  | .... | 8   | .... | 5.2   | ....                    | 5.16   | .... 5.10  |
| Nitrogen .....  | 1  | .... | 14  | .... | 9.2   | ....                    | 9.11   | .... 9.06  |
| <hr/>           |    |      |     |      |       |                         |        |            |
| Cinchonia ..... | 1  |      | 154 |      | 100.0 |                         | 100.00 | 100.00     |

*The salts of cinchonia* have been examined by Baup (*Ann. Ch. et Ph.*, xxvii. 323), and by Pelletier, Caventou, and Dumas. (*Ann. Ch. et Ph.*, xv. and xxiv.) Cinchonia completely neutralizes the acids, and forms salts which are mostly crystallizable and more soluble than the corresponding salts of quinia; they are bitter, insoluble in ether, and when in aqueous solution are rendered brown by tincture of iodine; they give white precipitates with the fixed alkalis, and with tincture of galls: they are rendered green by manganate of potassa.

*Sulphate of Cinchonia.* The *neutral sulphate*, obtained by dissolving cinchonia in excess of dilute sulphuric acid, and evaporating till a pellicle forms, crystallizes in rhomboidal octohedra, which in dry and warm air become opaque and efflorescent; they are soluble in less than their weight of water at 60°, and in alcohol, but not in ether.

They consist of

|                                    |   |      |     |      |       | Baup.       |
|------------------------------------|---|------|-----|------|-------|-------------|
| Cinchonia.....                     | 1 | .... | 154 | .... | 67.0  | .... 67.241 |
| Sulphuric acid .....               | 1 | .... | 40  | .... | 17.4  | .... 17.241 |
| Water .....                        | 4 | .... | 36  | .... | 15.6  | .... 15.518 |
| <hr/>                              |   |      |     |      |       |             |
| Crystallized sulphate of cinchonia | 1 |      | 230 |      | 100.0 | 100.000     |

*Subsulphate, or Disulphate of Cinchonia.* This salt is obtained by digesting excess of cinchonia in the dilute acid: it forms rhomboidal prisms containing 2 atoms of water of crystallization, which it loses when dried at 250°, and remains anhydrous, and may be fused. It is soluble in between 50 and 60 parts of water at 60°; and in about 6 parts

of alcohol, sp. gr. 0·85, and in 11 parts of absolute alcohol. It is insoluble in ether. The crystallized salt consists of

|  |   |     |     | Baup.  | Regnault.   |
|--|---|-----|-----|--------|-------------|
| Cinchonia .....                          | 2 | ... | 308 | 84·41  | } ... 95·26 |
| Sulphuric acid .....                     | 1 | ... | 40  | 10·91  |             |
| Water .....                              | 2 | ... | 18  | 4·68   | ... 4·74    |
| <hr/>                                    |   |     |     |        |             |
| Crystallized disulphate of cinchonia ... | 1 |     | 366 | 100·00 | 100·00      |

When excess of peroxide of lead is boiled in a solution of sulphate of cinchonia, and sulphuric acid added drop by drop till the filtered liquor tested by ammonia ceases to become turbid, carbonic acid escapes, and the liquor becomes deep-colored: if the operation be then stopped, any free acid removed by litharge, the solution evaporated to dryness, the dry mass treated by distilled water, and this solution by sulphuretted hydrogen, and then evaporated, a peculiar red or violet coloring matter is obtained, which Marchand terms *Cinchonetine*: it is bitter, deliquescent, soluble in water, alcohol, and sulphuric acid, but insoluble in ether: its aqueous solution is not disturbed by ammonia or potassa, but they gradually change its purple tint to a fawn color: subacetate of lead throws down a violet precipitate. The combined action of sulphuric acid and peroxide of lead resolves cinchonetine into colorless compounds. Analogous coloring matters are obtained from the other organic alkaloids. (*Journ. de Chimie Medicale*, July, 1844.)

*Chlorate of Cinchonia*, obtained by saturating chloric acid by cinchonia, forms clusters of white crystals. When heated, they first fuse and then explode.

*Hydrochlorate of Cinchonia*. Anhydrous cinchonia absorbs hydrochloric acid gas, and produces a neutral hydrochlorate, composed, according to Liebig, of

|                                  |   |     |     |       | Liebig. |
|----------------------------------|---|-----|-----|-------|---------|
| Cinchonia .....                  | 1 | ... | 154 | 80·6  | 81      |
| Hydrochloric acid .....          | 1 | ... | 37  | 19·4  | 19      |
| <hr/>                            |   |     |     |       |         |
| Hydrochlorate of cinchonia ..... | 1 |     | 191 | 100·0 | 100     |

*Dihydrochlorate of Cinchonia*. When cinchonia in excess is digested in dilute hydrochloric acid, a soluble salt, forming acicular crystals, is obtained, composed, according to Pelletier and Caventou, of

|                                  |   |     |     |       | Pelletier<br>and Caventou. |
|----------------------------------|---|-----|-----|-------|----------------------------|
| Cinchonia .....                  | 2 | ... | 308 | 89·3  | 89·5                       |
| Hydrochloric acid .....          | 1 | ... | 37  | 10·7  | 10·5                       |
| <hr/>                            |   |     |     |       |                            |
| Dihydrochlorate of cinchonia.... | 1 |     | 345 | 100·0 | 100·0                      |

*Iodate of Cinchonia* forms delicate prismatic crystals resembling amianthus.

*Nitrate of Cinchonia*. When very dilute nitric acid is saturated by cinchonia, a portion of the *nitrate* formed separates in the form of liquid globules, looking like oil, which, in the course of a few days, become groups of acicular crystals. This property belongs also to quinia, and may serve to distinguish these from other alkaloids.

*Phosphate of Cinchonia* is difficultly crystallizable; evaporated to



dryness it forms an opaque mass, which acquires a crystalline texture in water, and easily dissolves.

*Carbonate of Cinchonia.* This salt is said, by Thomson (*Org. Chem.*, 229), to be precipitated from the solutions of cinchonia by carbonated alkalis, and moist cinchonia is stated to absorb carbonic acid from the air, and then to effervesce when dissolved in acids.

*Arseniate of Cinchonia* is a very soluble, and difficultly-crystallizable salt.

*Tannate of Cinchonia* is thrown down in the form of a white precipitate on adding solution of tannic acid, or infusion of galls, to a neutral solution of cinchonia: it is soluble in excess of acid. The quantity of the precipitate occasioned by infusion of galls in decoctions of cinchonia is often resorted to as an indication of the proportion of alkaloid which they respectively contain. According to Henry, (*Journ. de Pharm.*, xxi. 221,) this tannate, dried at  $212^{\circ}$ , contains 27 per cent. of the alkaloid.

*Gallate of Cinchonia* is difficultly soluble in cold water, but hot water takes it up more readily, and the solution, as it cools, becomes first milky, but afterwards clears, and deposits the gallate in small crystalline grains.

*Oxalate of Cinchonia.* The neutral oxalate is difficultly soluble in cold water: it is rendered more soluble by excess of acid; it is thrown down when oxalate of ammonia is added to a neutral solution of a salt of cinchonia, in the form of a white powder, very sparingly soluble in hot water: this salt is soluble in hot alcohol, and part separates as the solution cools. It readily dissolves in oxalic acid.

*Tartrate of Cinchonia* is thrown down in the form of a somewhat difficultly soluble precipitate, on adding a solution of an alkaline tartrate to one of a neutral salt of cinchonia.

*Acetate of Cinchonia.* Acetic acid dissolves cinchonia: the solution is always acid; when partially evaporated it lets fall small crystals on cooling, which are neutral and difficultly soluble. When, on the contrary, the solution is evaporated to dryness, a gum-like mass is obtained, which is resolved by cold water into a soluble superacetate, and an insoluble subacetate.

*Cinchonate of Cinchonia.* This salt (see *Cinchonic Acid*,) forms very soluble acicular crystals of a silky lustre, containing about 20 per cent. of cinchonia. (HENRY and PLISSON. *Journ. de Pharm.*, xv. 406.)

2. QUINIA. Quinine.  $C_{20}H_{12}O_2N, = \overset{+}{Q}$ . Quinia is obtained from yellow bark (*Cinchona flava*; *Calisaya*; *Regia*,) by a process precisely similar to that for procuring cinchonia from pale bark. When quinia is obtained from the common varieties of yellow bark, it almost always contains more or less cinchonia: these alkaloids may be separated by solution in alcohol, which, when duly evaporated, deposits the cinchonia in crystals, while the quinia, being more soluble, remains in solution: by one or more repetitions of this process it may be freed from cinchonia: or if they are converted into *sulphates*, the sulphate of quinia being less soluble than the sulphate of cinchonia, crystallizes, and leaves the latter salt in solution.

Sulphate of quinia, which is abundantly prepared for medical use, is the most ready source of the alkaloid: it is obtained by adding ammonia

to a solution of that salt, when it falls in white flakes, which unless very carefully dried, are apt to become brown. Quinia is very difficult of crystallization, but it has been obtained in that form by very slowly evaporating its alcoholic solution by exposure to cold dry air. It may also be crystallized, according to Henry and Delondre (*Journ. de Pharm.*, xx. 157), by dissolving pure and crystallized sulphate of quinia in a large quantity of water, decomposing it by ammonia, washing the precipitate, dissolving it in weak alcohol, and adding water to the solution till it becomes milky: it is then left for some days exposed to the air, when portions of the separated quinia, which at first resembled fluid resin, gradually become crystalline, forming radiated and acicular groups, which are efflorescent. These crystals are *hydrate of quinia*; when heated they first soften, then become white and pulverulent, and, when fused, lose water; the fused quinia concretes into a resin-like mass, which, if cooled very slowly, shows signs of crystallization, and becomes negatively electric by friction: in water it gradually returns to the state of hydrate.

Quinia has a decided alkaline action upon proper tests; it is intensely bitter; very sparingly soluble, even in boiling water, of which it requires about 200 parts for its solution; it is readily soluble in boiling alcohol, which, when evaporated, leaves it in the form of a viscid mass, which indurates and acquires a resinous aspect on exposure to air. It is more soluble than cinchonia in ether. It forms distinct salts with the acids. When anhydrous quinia is heated in a tube, it fuses, becomes thick, viscid, and dark-colored, an oily liquid evaporates, ammoniacal and hydrocyanic vapors follow, and a bulky carbonaceous matter remains.

The equivalent of quinia is 162. It has been analysed by Pelletier and Caventou, by Dumas, (*Ann. Ch. et Ph.*, xxiv. 169); by Liebig, (*Traité de Chimie*, ii. 558, and *Poggend. Ann.*, xxi. 25); and by Henry and Plisson, (*Journ. de Pharm.*, xvii. 453); with the following results:

|                        |    |     |        |        | Pelletier and<br>Caventou. | Liebig. | Henry and<br>Plisson. |
|------------------------|----|-----|--------|--------|----------------------------|---------|-----------------------|
| Carbon .....           | 20 | 120 | 74·07  | 75·00  | 74·37                      | 74·55   |                       |
| Hydrogen .....         | 12 | 12  | 7·41   | 6·25   | 7·30                       | 8·43    |                       |
| Oxygen .....           | 2  | 16  | 9·88   | 10·00  | 9·73                       | 8·72    |                       |
| Nitrogen .....         | 1  | 14  | 8·64   | 8·75   | 8·60                       | 8·30    |                       |
| <hr/>                  |    |     |        |        |                            |         |                       |
| Anhydrous quinia ..... | 1  | 162 | 100·00 | 100·00 | 100·00                     | 100·00  |                       |

The *salts of quinia* are for the most part crystallizable, and are generally less soluble in water, and more bitter than the salts of cinchonia; they are also soluble in alcohol. Their aqueous solution has a peculiar opaline appearance, and they are liable to acquire a yellow or brown tint by long exposure to solar light.

*Sulphate of Quinia.* This salt has excited great attention on account of its medicinal importance, and it is manufactured both in this country and on the Continent, to a very great extent. Dumas estimates the annual export from Paris only, at 120,000 ounces. The quinia is obtained from yellow bark, and dissolved in dilute sulphuric acid: the first crops of the salt are decolorized by animal charcoal; it is again crystallized, and very carefully dried: this operation requires care, for if the desiccation is carried too far, the salt loses its crystalline character, and crumbles down into powder.



Many processes have been devised for the preparation of sulphate of quinia. The following is that of Henry Junr., which, according to Dumas, is generally adopted by the manufacturers in Paris. (*Chim. App. aux Arts*, v. 743.) The pulverised bark is boiled in from 8 to 10 parts of water acidulated by 12 *per cent.* of concentrated sulphuric acid, or better, by 25 *per cent.* of hydrochloric acid; after boiling for at least an hour, the decoction is strained off, and the residue submitted to a second and third ebullition in the same quantity of water, but with only half the quantity of the acid; the decoction should be continued till the residuary bark has lost all flavor. When the decoctions are cold, milk of lime is gradually added, under constant agitation, so as perfectly to neutralise the liquor, and leave slight excess of lime, which forms an insoluble compound with the coloring matter. When the liquor has thus been rendered alkaline, it becomes of a dirty grey color, and deposits a reddish grey flocculent precipitate, which when well formed is to be collected upon linen strainers, and subjected to gradual pressure, and the liquors which run off are collected in a vat, where they yield a farther deposit. The calcareous precipitates are then squeezed by means of a press, into a cake, which is to be treated by alcohol in order to separate the quinia; some dry the precipitate before subjecting it to the alcohol; others use it moist; in this latter case a stronger alcohol is required, but it penetrates more easily: if dried, the cake is pulverised and macerated in hot alcohol (sp. gr. 0.847). This operation is repeated (in close vessels in a water-bath) as long as the alcohol acquires color and bitterness; but the last liquors are put aside to be used for exhausting the fresh cakes. The stronger alcoholic liquors are then distilled so as to yield about three-fourths of the alcohol employed, and dilute sulphuric acid is added to the residue till it reddens litmus paper; this acid solution is then duly evaporated and left to cool, when in about 24 hours it is found concentered into a crystallized mass, which after having been drained is subjected to gradual pressure. The mother-liquors may be collected and again evaporated and crystallized, but it is better to dilute them and to precipitate the quinia by lime, and again treat the precipitate by alcohol and sulphuric acid, as in the first instance. The crude sulphate requires to be whitened by dissolving it in hot water and boiling it for a few minutes with animal charcoal; it should then be quickly filtered into proper vessels for crystallization, a very little sulphuric acid being sometimes added to facilitate that process, which is usually complete in 24 hours. The salt is then drained and dried, which latter operation requires much care in order to prevent efflorescence.

The preceding process requires a large quantity of alcohol, and various means have been suggested for the purpose of avoiding the use of that expensive solvent, amongst which Pelletier's patented process is, according to Dumas, the best; it consists in treating the dry cakes of quinia and lime with oil of turpentine instead of alcohol, which dissolves the quinia. This solution, agitated with water acidulated by sulphuric acid, abandons the quinia, which becomes converted into sulphate. By repose, the oil floats and may be again employed, whilst the sulphate is evaporated as usual. It appears, however, that by this process about one-twentieth less of quinia is obtained than by the preceding, so that on that account it is not adopted. Indeed, according to Pereira, even in this country, the

use of alcohol does not, on the large scale, add much more than a penny an ounce to the cost of the disulphate, as the greater part of it is recovered.

There are two other processes which have been suggested, but they are far less productive than that just described. The one, by Badollier, which consists in boiling for 15 minutes, 1 part of bruised bark, in 8 parts of water rendered alkaline by potassa; the decoction is then allowed to cool, and the whole pressed out in a strainer; the residue is washed and pressed again; and then, the bark thus lixiviated, is gently heated with water, to which hydrochloric acid is gradually added, so as to render it acid; it is then raised to the boiling-point, strained, and sulphate of magnesia added; the liquor is then precipitated by caustic potassa, and the precipitate when dry treated by alcohol and sulphuric acid. The other process is that of Stoltze; 1 part of the pulverised bark is boiled in 6 of water, with the addition of lime; the whole is then thrown upon a strainer, and the pressed bark is digested with a quantity of hydrochloric acid and water, the acid being equal to about a sixteenth part of the weight of the bark; the liquor is filtered, concentrated, and precipitated by caustic potassa, which throws down a mixture of lime and quinia, which may be separated by alcohol, or even directly, by dilute sulphuric acid. The object of these processes is to abstract the acids, coloring matters, gum, &c., from the barks, and to leave in them the alkaloids; but they do not answer upon the large scale.

The process for obtaining sulphate of quinia directed in the *London Pharmacopœia*, which is in fact that of Henry and Plisson, (*Ann. Ch. et Ph.*, xxxv. 165,) is as follows:

“Take of Heart-leaved Cinchona, bruised, lb. vij.; Sulphuric Acid, ℥ix.; Purified Animal Charcoal, ℥ij.; Hydrated Oxide of Lead, Solution of Ammonia, Distilled Water, each as much as may be sufficient. Mix four ounces and two drachms of the sulphuric acid with six gallons of distilled water, and add the cinchona to them; boil for an hour, and strain. In the same manner again boil what remains in acid and water, mixed in the same proportions, for an hour, and again strain. Finally, boil the cinchona in eight gallons of distilled water for three hours, and strain. Wash what remains frequently with boiling distilled water. To the mixed liquors add oxide of lead, while moist, nearly to saturation. Pour off the supernatant liquor, and wash what is thrown down with distilled water. Boil down the liquors for a quarter of an hour, and strain; then gradually add solution of ammonia to precipitate the quinia. Wash this until nothing alkaline is perceptible. Let what remains be saturated with the rest of the sulphuric acid, diluted. Afterwards digest with two ounces of animal charcoal, and strain. Lastly, the charcoal being thoroughly washed, evaporate the liquor cautiously, that crystals may be produced.”

The directions of the Edinburgh College are as follow:

“Take of yellow bark, in coarse powder, one pound; carbonate of soda, eight ounces; sulphuric acid, half a fluid ounce; purified animal charcoal, two drachms. Boil the bark for an hour in four pints of water, in which half the carbonate of soda has been dissolved; strain and express strongly through linen or calico; moisten the residuum with water, and express again, and repeat this twice. Boil the residuum for



half an hour with four pints of water and half the sulphuric acid; strain, express strongly, moisten with water, and express again. Boil the residuum with three pints of water and a fourth part of the acid; strain and squeeze as before. Boil again the residuum with the same quantity of water and acid, strain and squeeze as formerly. Concentrate the whole acid liquids to about a pint; let the product cool; filter it, and dissolve in it the remainder of the carbonate of soda. Collect the impure quinia on a cloth, wash it slightly, and squeeze out the liquor with the hand. Break down the moist precipitate in a pint of distilled water; add nearly one fluid scruple of sulphuric acid, heat it to  $212^{\circ}$ , and stir occasionally. Should any precipitate retain its gray color, and the liquid be neutral, add sulphuric acid, drop by drop, stirring constantly, till the gray color disappears. Should the liquid redden litmus, neutralize it with a little carbonate of soda. Should crystals form on the surface, add boiling distilled water to dissolve them. Filter through paper, preserving the funnel hot; set the liquid aside to crystallize; collect and squeeze the crystals; dissolve them in a pint of distilled water heated to  $212^{\circ}$ ; digest the solution for fifteen minutes with the animal charcoal; filter, and crystallize as before. Dry the crystals with a heat not exceeding  $140^{\circ}$ .

“The mother-liquors of each crystallization will yield a little more salt by concentration and cooling.”

The object of this process is to extract, by means of the solution of carbonate of soda, the acids, the coloring and extractive matters, the gum, &c. from the bark, but leaving the cinchona alkaloids. Stoltze used for this purpose lime, Badollier and Scharlau caustic potash. The alkaline decoction has a very deep color. By boiling the residuum in water acidulated with sulphuric acid, the alkaloids are dissolved. On the addition of carbonate of soda, double decomposition takes place, and the impure quinia is precipitated. This is afterwards dissolved in water acidulated with sulphuric acid, and the filtered liquid set aside to crystallize. The impure disulphate of quinia thus obtained is re-dissolved in boiling water, and the solution, after being decolorized by digestion with animal charcoal, is filtered, and put aside to crystallize.

Sulphate of quinia, as it occurs in commerce, is at present regarded as a subsalt, or a *Disulphate*, and is such, in reference to the above equivalent of quinia; but by some, the equivalent of quinia has been doubled, so as to represent this as a neutral sulphate.

*Disulphate of Quinia* may be obtained in long acicular crystals, but it is generally in delicate fibrous and soft crystals of a pearly aspect, and flexible like amianthus; it is efflorescent, intensely bitter, and requires about 740 parts of cold, and 30 parts of boiling water, for solution. It is soluble in 80 parts of cold alcohol, (sp. grav. 0.850), and much more soluble in boiling alcohol. This salt readily fuses, looking at first like melted wax; it then reddens, and begins to be decomposed; in the air it burns, producing at first a bulky charcoal, which, by continued heat, is consumed without residue. It has the curious property of becoming luminous when heated to about  $212^{\circ}$ ; its phosphorescence is increased by friction, and electricity is, at the same time, manifest.

This salt is subject to various adulterations; the substances said to be employed for this purpose are, water, sugar, gum, starch, ammoniacal salts,

and earthy salts, such as sulphate of lime, sulphate of magnesia, and acetate of lime; and lastly, salicine, and sulphate of cinchonia. Pure sulphate of quinia, when heated to  $212^{\circ}$  to deprive it of its water of crystallization, should lose only from 8 to 10 *per cent.* in weight. *Sugar* may be detected by dissolving the suspected salt in water, and adding precisely so much carbonate of potassa as will precipitate the quinia. The taste of the sugar, no longer obscured by the bitter of the quinia, will generally be perceived; and it may be separated from the sulphate of potassa by evaporating gently to dryness, and then dissolving the sugar by boiling alcohol. *Gum*, and *starch*, are left when the impure sulphate of quinia is digested in strong alcohol. *Ammoniacal salts* are discovered by the strong odor of ammonia which may be observed when the sulphate is put into a warm solution of potassa. *Earthy salts* may be detected by burning a portion of the sulphate, which, when pure, leaves no residue. (PHILLIPS. *Phil. Mag. and Ann.*, iii. 111, and TURNER'S *Elements*.) According to Dumas, *margaric acid* is sometimes mixed with sulphate of quinia; it is detected by its insolubility in dilute hydrochloric acid. Dr. Nevil's tests for *sugar* and *salicine*, are as follow: to 2 grains of the suspected salt add 4 drops of sulphuric acid and 8 of water; if fatty matter or starch be present, they remain; if absent, the salt is dissolved, and on applying heat, sugar is indicated by *charring*, and salicine by a *red color*; pure sulphate of quinia is not affected by this application of sulphuric acid. (*Pharm. Journ.*, v. 75.) Dr. Pereira observes, that sulphate of cinchonia may be made to crystallize in a pulverulent form by stirring the solution, and may in that state be readily intermixed with sulphate of quinia, a fraud as he supposes sometimes carried on to a considerable extent. To detect it, precipitate a solution of the suspected salt in water, by potassa; collect the precipitate, and boil it in alcohol; the cinchonia crystallizes as the liquor cools, while the quinia remains in the mother-liquor. (*Mat. Med.*, p. 142.) According to Bouchardat, a good test of the presence of sulphate of quinia in solution, is the ioduretted iodide of potassium: it has been applied by Robert to its detection in the urine, which, in patients who are taking the sulphate, often contains it in very tangible quantity: 4 parts of iodide of potassium, 1 of iodine, and 10 of water, are the proportions recommended: it gives a yellowish brown insoluble precipitate, which "is a double iodide of potassium and quinia: it is decomposed by dilute sulphuric acid, and resolved into sulphate of potassa and sulphate of quinia, iodine being precipitated:" Robert suggests this as a means of reobtaining quinia from the urine of patients who are under a course of the sulphate. (*Journ. de Pharm.*, Septembre, 1843.)

The accurate determination of the composition of this salt, in its various states, is interesting and important; upon this subject there is some difference in the statements of different authors: the following, as given by Dumas and Baup, agrees with my own observations, but Liebig does not admit the existence of an anhydrous basic sulphate, which ought to consist of

|                                      |   |      |     |      |     |      | Baup. |
|--------------------------------------|---|------|-----|------|-----|------|-------|
| Quinia .....                         | 2 | .... | 324 | .... | 89  | .... | 89.1  |
| Sulphuric acid .....                 | 1 | .... | 40  | .... | 11  | .... | 10.9  |
| <hr/>                                |   |      |     |      |     |      |       |
| Anhydrous disulphate of quinia ..... | 1 |      | 364 |      | 100 |      | 100.0 |



The *ordinary sulphate of quinia*, or the *crystallized disulphate*, consists of

|  |   |      |     |      |       |           |
|--|---|------|-----|------|-------|-----------|
|  |   |      |     |      |       | Dumas.    |
| Quinia .....                           | 2 | .... | 324 | .... | 74.3  | .... 74.6 |
| Sulphuric acid.....                    | 1 | .... | 40  | .... | 9.2   | .... 9.1  |
| Water .....                            | 8 | .... | 72  | .... | 16.5  | .... 16.3 |
| <hr/>                                  |   |      |     |      |       |           |
| Crystallized disulphate of quinia .... | 1 |      | 436 |      | 100.0 | 100.0     |

When the salt effloresces, or when dried at 212°, it loses 4 atoms of its water, and when dried at 240° it loses 6 atoms, retaining 2, which, according to Baup, may be expelled by a higher temperature, but which are retained, according to Liebig, till the salt decomposes. Liebig also states that in efflorescing in dry air, disulphate of quinia loses three-fourths of its water of crystallization ; that is to say, 10.75 *per cent*.

*Neutral sulphate of Quinia.* When the disulphate of quinia is triturated with dilute sulphuric acid, it first forms a white magma, which afterwards dissolves on adding more of the acid, and on evaporating this solution, or, if concentrated, on leaving it at rest, prismatic crystals of the *neutral sulphate* (according to our equivalent) are formed. This salt is much more soluble than the preceding, and at 212° it fuses in its water of crystallization ; when dissolved in alcohol its solution yields crystals which fall to powder on exposure to air. This sulphate, in crystals, is composed, according to Dumas, of

|                                       |   |      |     |      |       |           |
|---------------------------------------|---|------|-----|------|-------|-----------|
|                                       |   |      |     |      |       | Dumas.    |
| Quinia .....                          | 1 | .... | 162 | .... | 59.1  | .... 59.4 |
| Sulphuric acid.....                   | 1 | .... | 40  | .... | 14.6  | .... 14.3 |
| Water .....                           | 8 | .... | 72  | .... | 26.3  | .... 26.3 |
| <hr/>                                 |   |      |     |      |       |           |
| Crystallized sulphate of quinia ..... | 1 |      | 274 |      | 100.0 | 100.0     |

The various sulphates of quinia, therefore, may be thus represented :

1. Anhydrous disulphate .....

2. Crystallized disulphate .....

3. Effloresced disulphate .....

4. Ditto, dried at 240° .....

5. Anhydrous sulphate .....

6. Crystallized sulphate .....
- +

+

+

+

+

+
- Q<sub>2</sub> SO<sub>3</sub>

Q<sub>2</sub> SO<sub>3</sub> + 8HO

Q<sub>2</sub> SO<sub>3</sub> + 4HO

Q<sub>2</sub> SO<sub>3</sub> + 2HO

Q SO<sub>3</sub>

Q SO<sub>3</sub> + 8HO

*Hyposulphate of Quinia* is obtained by double decomposition, from solutions of sulphate of quinia and hyposulphate of baryta : it is easily crystallizable, and less soluble in water than the sulphate.

*Chlorate of Quinia*, obtained by saturating aqueous chloric acid with quinia, and concentrating the solution, forms acicular tufts. When heated, it first fuses, and is then suddenly decomposed with explosion.

*Hydrochlorate of Quinia.* When dry quinia is exposed to a current of hydrochloric acid gas, it absorbs 18 *per cent.*, and forms a salt more soluble than the sulphate. (LIEBIG.) This salt probably consists of

|                                   |   |      |     |      |       |      |                 |
|-----------------------------------|---|------|-----|------|-------|------|-----------------|
| Quinia.....                       | 1 | .... | 162 | .... | 81.4  | .... | Liebig.<br>81.9 |
| Hydrochloric acid .....           | 1 | .... | 37  | .... | 18.6  | .... | 18.1            |
| <hr/>                             |   |      |     |      |       |      |                 |
| Anhydrous hydrochlorate of quinia | 1 |      | 199 |      | 100.0 |      | 100.0           |

When quinia is dissolved in hydrochloric acid, the solution affords nacreous crystals on evaporation, which are more soluble than sulphate of quinia, and less soluble than hydrochlorate of cinchonia; they contain about 7 per cent. of hydrochloric acid. (PELLETIER and CAVENTOU.) This is a *basic hydrochlorate of quinia*: it is best obtained, according to Winckler, by mixing 480 parts of effloresced disulphate of quinia, and 139 of crystallized chloride of barium, with water, and keeping the mixture for some time at a temperature of 104°: it should then be filtered and evaporated for crystallization, at the same temperature; it forms white acicular and nacreous crystals, sparingly soluble in water, composed of

|   |   |      |     |      |        |
|---|---|------|-----|------|--------|
| Quinia .....                                | 2 | .... | 324 | .... | 83.50  |
| Hydrochloric acid .....                     | 1 | .... | 37  | .... | 9.53   |
| Water .....                                 | 3 | .... | 27  | .... | 6.97   |
| <hr/>                                       |   |      |     |      |        |
| Crystallized dihydrochlorate of quinia .... | 1 |      | 388 |      | 100.00 |

When a solution of corrosive sublimate is added to a solution of hydrochlorate of quinia a curdy double salt falls in white flakes, which easily fuses when heated. In the same way, a solution of bichloride of platinum throws down a yellow double salt in the form of a crystalline powder; it requires 1500 parts of cold, and 120 of boiling water for solution. Alcohol only dissolves one-2000th of its weight. It consists of 45.77 bichloride of platinum, and 54.23 hydrochlorate of quinia. (LIEBIG.) The same compound may be obtained by adding the bichloride of platinum to any other solution or salt of quinia mixed with hydrochloric acid.

*Iodate of Quinia* is obtained by saturating aqueous iodic acid by quinia, and evaporating for crystallization; it forms brilliant silky needles resembling the sulphate. Its aqueous solution furnishes a precipitate of a very slightly soluble acid salt, on the addition of free iodic acid. Iodic acid also precipitates the other salts of quinia. When this iodate is heated it explodes. Serullas has proposed its employment in medicine.

*Nitrate of Quinia.* When quinia is dissolved in diluted nitric acid, and the solution evaporated, the nitrate separates in the form of an oil-like liquid, which gradually crystallizes. (PELLETIER. CAVENTOU. DUMAS.)

*Phosphate of Quinia* is easily crystallizable; it forms acicular prisms, very soluble in water and in alcohol. (PELLETIER and CAVENTOU.) This salt has been by some preferred to the sulphate in the treatment of intermittents.

*Ferrocyanide of Quinia.* This salt is prepared as follows: 2 parts of finely pulverized disulphate of quinia is mixed with 3 parts of ferrocyanide of potassium, previously dissolved in six times its weight of water; this mixture is repeatedly agitated whilst heating up to the boiling-point, when a greenish-yellow matter, of an oily consistence, falls to the bottom. Decant off the liquid, wash the deposit with cold water, and dissolve it



in alcohol, filter and evaporate. The salt is deposited in confused crystals, of a greenish-yellow color, and very bitter taste: its alcoholic solution is precipitated by water. It has succeeded as a febrifuge where sulphate of quinia failed. (BERTOZZI, *Journ. de Pharm.*, xix. 45.)

*Arseniate of Quinia* much resembles the appearance of the phosphate, but its crystals are less nacreous. (PELLETIER and CAVENTOU.)

*Tannate of Quinia.* The infusion and tincture of galls precipitate quinia from its solutions: pure tannic acid produces a similar effect: the precipitate is soluble in acetic acid, and difficultly so in water. It contains according to O. Henry, 28.5 per cent. of quinia. (*Journ. de Pharm.*, xxi. 221.)

*Gallate of Quinia.* Gallic acid occasions precipitates in all the solutions of quinia which are not very dilute; the alkaline gallates are yet more effective precipitants. Gallic acid unites directly with quinia, and the salt is difficultly soluble in cold water; its solution in boiling water becomes milky as it cools. The gallate of quinia is soluble in alcohol, and in excess of acid. (DUMAS.)

*Oxalate of Quinia.* When a concentrated solution of oxalic acid is added to one of a soluble salt of quinia, a precipitate of oxalate of quinia falls; it dissolves in boiling water, and yields nacreous acicular crystals on cooling; it dissolves in excess of oxalic acid, and this solution also crystallizes in needles: the neutral oxalate is very soluble in alcohol, and the hot alcoholic solution deposits crystals on cooling. This oxalate is most readily prepared by double decomposition.

*Tartrate of Quinia* resembles the oxalate, but is more soluble.

*Citrate of Quinia* is prepared by decomposing the disulphate of quinia by acid citrate of soda; it crystallizes in bitter needles, sparingly soluble in water: it is occasionally used in medicine.

*Acetate of Quinia.* The acetate of quinia, when slightly acid, is easily crystallizable: the solution, when evaporated to a certain point, forms a mass of distinct acicular crystals; when very slowly evaporated, it yields peculiar mamillary and stellated groups; it is not very soluble, and if colored, it may be washed in water, and subsides in silky filamentous crystals; its concentrated solution in boiling water, concretes into a crystalline mass when cold.

**QUINOLINE. CINCHOLINE.** When quinia or cinchonia (or strychnia) are distilled with caustic potassa, an oily liquid is obtained to which the above name has been given. It is bitter, alkaline, and forms crystallizable salts with the acids. Its sp. gr. is 1.084. Its formula is  $C_{19}H_8N$ . In its production from quinia, hydrogen is evolved and carbonate of potassa formed; so that  $C_{20}H_{12}O_2N + KO = C_{19}H_8N + KO, CO_2, + H_4$ . Quinoline requires a high temperature for its volatilisation and is easily decomposed, but when distilled with water, it passes over without alteration. The presence and formation of quinoline may be ascertained by its peculiar odor, which resembles that of St. Ignatius' bean. Cinchonia affords it more readily than the other alkaloids. (GERHARDT, *Ann. Ch. et Ph.*, 3ème Sér., vii. 251.)

The following comparative table of the principal distinctive characters of cinchonia and quinia is from Dr. Pereira's *Elements of Materia Medica*.

|  | CINCHONIA.   | QUINIA.   |
|--|--|---|
| <i>Form</i> .....  | Crystalline.   | Amorphous (in the anhydrous state). The hydrate is crystallizable, but with difficulty. |
| <i>Taste</i> .....   | Bitter.  | Very bitter.  |
| <i>Fusibility</i> .....  | Infusible when quite dry; when moist fuses, but at the same time decomposes. | Fusible.  |
| <i>Composition</i> .....   | 1 atom contains only 1 atom of oxygen.                                       | 1 atom contains 2 atoms of oxygen.  |
| <i>Combining proportion, or atomic weight</i> .... }                                 | 154  | 162   |
| <i>Solubility</i> { in water .....   | Dissolves in 2500 times its weight of boiling water.                         | Dissolves in 200 times its weight of boiling water.                                     |
| { in alcohol .....   | Soluble; solution readily crystallizes.                                      | More soluble than cinchonia; solution with difficulty crystallizes.                     |
| { in ether .....   | Sparingly soluble; solution readily crystallizes.                            | Very soluble; solution crystallizes with difficulty.                                    |
| <i>Salts.</i> {  | <i>Disulphate</i> { form and aspect .....                                    | Pearly silky needles.   |
|  | { solubility ..  | Soluble in 740 parts of cold water or 80 parts of spirit (sp. gr. 0·85).                |
|  | <i>Neutral Sulphate</i> .....  | Soluble in 11 parts of cold water. More soluble in spirit than sulphate of cinchonia.   |
|  | <i>Hydrochlorate</i> .....   | Crystallizes in silky or pearly tufts.  |
|  | <i>Phosphate</i> .....   | Crystallizes in pearly needles.   |
|  | <i>Arseniate</i> .....   | Crystallizes in prismatic needles.  |
| <i>Acetate</i> .....   | Very soluble; crystals small and granular.                                   | Less soluble; crystals in silky tufts, grouped in stars, &c.                            |
| The solution of <i>disulphate</i> treated by chlorine, then by ammonia, yields ..... | A reddish solution.  | An emerald-green solution.  |

3. ARICINA. This alkaloid was discovered in 1829, by Pelletier and Coriol, (*Journ. de Pharm.*, xv. 575,) in a bark from Arica, which had been fraudulently mixed with cinchonia: in appearance it resembles *yellow bark*, but we are unacquainted with its botanical history. Treated as usual for the separation of its alkaloid, it yields a substance much resembling cinchonia in its external characters, but differing from it materially in its aggregate chemical properties. It is insoluble in water, and nearly tasteless, but, after a time, produces a biting sensation upon the palate; its acid solutions are very bitter; heated, it fuses like quinia, and is not volatile. It is more soluble in alcohol than cinchonia, and is especially distinguished from cinchonia by its solubility in ether.

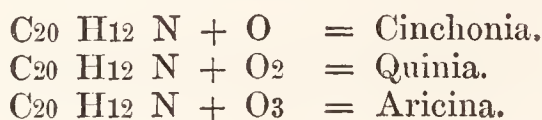
The salts of aricina are very bitter, very soluble in water and in alcohol, and insoluble in ether. Its *sulphate* is not crystallizable from its aqueous solution, but yields a gelatinous mass, becoming horny when dried: its alcoholic solution, on the contrary, affords silky crystals, much like sulphate of quinia. When a few drops of sulphuric acid are added to its gelatinous sulphate, another sulphate, crystallizable in flattened prisms, is formed. The action of nitric acid on *aricina* is very distinct; when concentrated, it produces with it a very deep green color; when



more dilute the color is lighter, and when very dilute the solution is colorless: the production of the green color is accompanied by a decomposition of the alkaloid, but by using a very dilute acid for its solution, this is prevented, and a colorless nitrate obtained. According to Pelletier, the ultimate components of aricina are

|                |    |       |     |       | Pelletier. |
|----------------|----|-------|-----|-------|------------|
| Carbon .....   | 20 | ..... | 120 | ..... | 70·6       |
| Hydrogen ..... | 12 | ..... | 12  | ..... | 7·1        |
| Oxygen .....   | 3  | ..... | 24  | ..... | 14·1       |
| Nitrogen ..... | 1  | ..... | 14  | ..... | 8·2        |
| <hr/>          |    |       |     |       |            |
| Aricina .....  | 1  |       | 170 |       | 100·0      |

It is remarked by Pelletier, that cinchonia, quinia, and aricina, may be regarded as oxides of a common radical or base, represented as follows:



The atomic constitution of these, and of the preceding alkaloids, suggests many theoretical views, which, however, have not been sufficiently matured to merit a place here, and are essentially dependent upon the equivalents by which they are represented. The numbers which I have adopted represent these bodies as *nitrurets* of a compound radical, or as consisting of carbon, hydrogen, and oxygen + 1 atom of nitrogen; hence the notion of the existence in them of ammonia, to which, even their alkaline characters have been by some ascribed: Dumas compares them to urea, and regards them as amides; but these hypotheses are all unsatisfactory, and till our knowledge of the various hydrocarbons, and of their combinations, is much extended and simplified, we shall probably not be able to frame any correct theory applicable to the constitution of these highly interesting compounds.

4. QUINOIDINE. Sertuerner has given this name to an alkaloid which accompanies the others, in yellow and red cinchona. Liebig quotes several authorities, and among others, Henry and Delondre, and Guibourt, (*Journ. de Pharm.*, Mars, 1830, p. 144; *Journ. de Chim. Med.*, Juin, 1830, p. 353,) showing that a peculiar alkaloid had been frequently remarked in the uncrystallizable mother-liquors derived from the preparation of cinchonia and quinia. According to Sertuerner, quinoidine may be precipitated in the form of a brown resin-like matter, fusible, and bitter as quinia; it is almost insoluble in water, and fuses in boiling water, its solution exhibiting nearly the same characters as that of quinia. It is very soluble in alcohol, and ether throws brown flocks from the alcoholic solution. It neutralises the acids, and produces with them brown, viscid, bitter, and uncrystallizable compounds, very soluble in water and in alcohol. According to Koch, 128 parts of dry quinoidine saturate 20 parts of concentrated sulphuric acid.(?) When the quinoidine had been previously exhausted by ether, 120 parts of it saturated the same quantity of acid, so that the saturating power of quinoidine is greater than that of cinchonia and of quinia; it is evident, however, that these experiments require repetition.

5. CINCHONIC ACID. KINIC ACID. QUINIC ACID.  $C_7H_5O_5, HO=\overline{Q} + HO$ . This acid, originally noticed by Hofmann, and by Vauquelin (*Ann. de Ch.*, lix. 162), is contained in the different species of *cinchona*, combined with lime, and with their alkaloids. In the preparation of quinia and cinchonia, where the bark is digested in dilute sulphuric acid and the alkaloids are thrown down by lime, *cinchonate of lime* remains in the liquor: when this is filtered, and evaporated to dryness in a water-bath, an extract is obtained from which alcohol abstracts certain soluble matters, and leaves the impure cinchonate; it must be again dissolved in water, and the solution decolorized by digestion with animal charcoal, when on filtering and evaporating, it yields crystals of cinchonate of lime. To decompose this salt, and separate the cinchonic acid, two methods have been pursued. One consists in the use of oxalic acid, but it is apt to leave the cinchonic acid impure from the presence of a little oxalate of potassa; the other therefore is preferable, in which the solution of cinchonate of lime is decomposed by basic acetate of lead, and the precipitate, which is a basic cinchonate of lead, is then washed, and decomposed by sulphuretted hydrogen; the acid liquor is then filtered off, and carefully evaporated by a very gentle heat, and afterwards left to spontaneous evaporation, when crystals are slowly formed. These must be separated from the mother-liquor, redissolved in a little boiling water, and the solution evaporated *in vacuo* over sulphuric acid, when colorless crystals are obtained. (See, in reference to this acid, HENRY and PLISSON, *Journ. de Pharm.*, xiii. 268, and xv. 389; LIEBIG and BAUP, *Ann. Ch. et Ph.*, xlvii. 188, and li. 56; also WOSKRESENSKY, *Repert. de Chimie*, v. 233.)

Cinchonic acid crystallizes in groups of rhombic prisms, not unlike those of tartaric acid. It has a powerful and pure acid taste. At about  $310^\circ$  it fuses, and on cooling concretes into a transparent amorphous mass; it is decomposed at a higher temperature, and is not volatile; it dissolves in between 2 and 3 parts of cold water, and is much more soluble in boiling water. It is very sparingly soluble in absolute alcohol, but readily dissolves in common spirit of wine. It is very little soluble in ether. It has been analysed by Baup, and by Liebig, with discrepant results; the most recent analysis is by Woskresensky, from which Berzelius deduces for the *anhydrous acid*, the formula  $C_7H_5O_5$ ; and represents *the crystallized acid* as  $C_7H_5O_5 + HO$ .

|                               |   |    |        |         | Woskresensky. | Liebig. | Baup. |
|-------------------------------|---|----|--------|---------|---------------|---------|-------|
| Carbon .....                  | 7 | 42 | 48.28  | 48.320  | 46.23         | 50.0    |       |
| Hydrogen.....                 | 5 | 5  | 5.75   | 5.734   | 5.89          | 5.6     |       |
| Oxygen.....                   | 5 | 40 | 45.97  | 45.946  | 47.88         | 44.4    |       |
| <hr/>                         |   |    |        |         |               |         |       |
| Anhydrous cinchonic acid .... | 1 | 87 | 100.00 | 100.000 | 100.00        | 100.0   |       |

The components of the crystallized acid are

|  |   |    |        |       |                                     |   |    |        |
|--|---|----|--------|-------|-------------------------------------|---|----|--------|
| Carbon .....                           | 7 | 42 | 43.75  | } = { | Anhydrous cincho-<br>nic acid ..... | 1 | 87 | 90.62  |
| Hydrogen .....                         | 6 | 6  | 6.25   |       |                                     |   |    |        |
| Oxygen .....                           | 6 | 48 | 50.00  |       |                                     | 1 | 9  | 9.38   |
| <hr/>                                  |   |    |        |       |                                     |   |    |        |
| Crystallized cin-<br>chonic acid ....} | 1 | 96 | 100.00 |       |                                     | 1 | 96 | 100.00 |

*Cinchonates. Quinates.* These salts are mostly soluble, and may be obtained in crystals by very slow or spontaneous evaporation. When



their solutions are rapidly evaporated, they leave a gum-like residue, which resumes a saline aspect when moistened. They are insoluble in absolute alcohol. These salts are recognised by the production of *chinone* or *quinone*, when their solution is mixed with a little finely-pulverized peroxide of manganese, to which a quantity of oil of vitriol is then added, and the mixture distilled.

*Chinone* forms a sublimate of golden-colored crystals, soluble in water, very volatile, and having a very peculiar distinctive odor. Their formula, according to Woskresensky, is  $C_{25}H_8O_8$ . (WÖHLER, *Chem. Gaz.*, 1844, p. 490.) When hydriodic acid is added to a saturated solution of chinone, it immediately becomes brown, from the separation of iodine, and on evaporating the filtered liquor, colorless crystals of *hydrochinone* are obtained, which are immediately rendered brown by ammonia, and dark-yellow by acetate of copper. These crystals are constituted of the elements of chinone + 4 atoms of hydrogen, their formula being  $C_{25}H_{12}O_8$ .

*Hydrochinone* is the chief product of the distillation of cinchonic acid; it may also be prepared by acting upon a saturated solution of chinone, in which some chinone is also suspended, by sulphurous acid. When hydrogen is abstracted from the colorless hydrochinone, or when chinone itself combines with hydrogen, *green hydrochinone* is the result. It separates in a crystalline state, coloring the liquid for the moment blackish-red, and then forming brilliant green prisms with a metallic lustre. It is most readily obtained by mixing the solution of colorless hydrochinone with perchloride of iron, or by adding a few drops only of sulphurous acid to a solution of chinone. The formula of the green hydrochinone is  $C_{12}H_{10}O_8$ , so that it is intermediate in composition between chinone and colorless hydrochinone, and may, in fact, be obtained by mixing their solutions. Wöhler has described several other compounds obtained by the action of chlorine, hydrochloric acid, and sulphuretted hydrogen, upon the preceding substances. The odor of chinone is so distinct that, according to Stenhouse (*Mem. Chem. Soc.*, ii. 226,) it enables us to detect the presence of cinchonic acid, and so to facilitate the discrimination of true from spurious cinchonas. "To examine a bark for kinic (cinchonic) acid, it is merely necessary to boil a little of it with slight excess of lime, to pour off and concentrate the liquor, introduce it into a retort, and distil it with a mixture of half its weight of sulphuric acid and of peroxide of manganese. If the bark contains the smallest quantity of kinic acid, the first portion of the liquid which distils over has a yellow color, and the very peculiar smell of chinone. If the liquid is treated with a little ammonia, it immediately becomes of a deep brown color, which in a few minutes changes to brownish-black; or if a little solution of chlorine is added to the liquid, it changes to a bright-green color. The distillation need not be long continued, as the chinone, being very volatile, passes nearly all over at first. I have tried this experiment with genuine barks, and have readily detected the kinic acid when less than a quarter of an ounce of each was employed; I have also operated on 2 ounces of false bark (*China nova Surinamensis*), and have detected no trace of kinic acid. According to Berzelius, kinic acid exists in the bark of *Pinus sylvestris*, and other trees; but I have been unable to detect any trace of it, though on adding less than 2 grains of kinate of lime, the presence of chinone in the

liquid which distilled over was immediately perceptible. The presence of cinchonia or quinia in a bark, may be detected by macerating it with dilute sulphuric acid, precipitating the infusion by slight excess of carbonate of soda, and distilling the precipitate with excess of caustic soda or potassa, when *cincholine* will distil over in oily drops, if the bark contained either of the alkaloids. Cincholine is recognizable by its peculiar taste and smell, and its strongly marked alkaline properties. It is nearly insoluble in water, unless first neutralized by an acid, when it readily dissolves, but it is immediately re-precipitated in oily drops by the addition of an alkali. It is true that cincholine may also be produced by other alkaloids, as for instance by strychnia, but its production clearly indicates the presence of an alkaloid in the bark, the exact nature of which may be subsequently ascertained by the usual methods."

*Cinchonate of Ammonia* is deliquescent, and becomes sour on evaporation.

*Cinchonate of Potassa* is bitter and deliquescent.

*Cinchonate of Soda* forms hexahedral prisms, permanent in the air, and soluble at  $60^{\circ}$  in half its weight of water. The crystals include 14.5 per cent. of water. (BAUP.)

*Cinchonate of Lime.* This salt crystallizes in transparent rhomboids, soluble in 9 parts of water at  $60^{\circ}$ , and much more soluble in hot water: when dried at  $212^{\circ}$ , it loses 29.5 per cent. of water, and may then be dried at  $288^{\circ}$ , without further loss of weight. According to Berzelius, a small quantity of cinchonate of lime may be extracted from the alburnum of fir-trees, but Stenhouse failed in detecting it.

*Cinchonate of Baryta* crystallizes in six-sided prisms, which become opaque in the air, are very soluble in water, very sparingly soluble in alcohol, and contain 17.42 per cent. of water of crystallization.

*Cinchonate of Strontia* forms tabular crystals soluble in 2 parts of water at  $55^{\circ}$ , and including 27.95 per cent. of water, which escapes by efflorescence, on exposure to air.

*Cinchonate of Magnesia* forms very soluble tufted crystals.

*Cinchonate of Manganese* forms lamellar rose-colored crystals.

*Cinchonate of Peroxide of Iron* forms an orange-colored gum-like mass.

*Cinchonate of Zinc* forms lamellar and tufted crystals.

*Cinchonate of Nickel* is a very soluble green gum-like salt.

*Cinchonate of Copper* crystallizes in green needles and rhomboidal tables, which whiten upon the surface when exposed to air. According to Liebig, the best crystals are obtained by exposing a solution to spontaneous evaporation, formed by decomposing sulphate of copper by cinchonate of baryta. The formula of this salt, after having been dried at  $310^{\circ}$ , is  $\text{CuO}, \text{C}_7 \text{H}_5 \text{O}_5$ . There appears also to be a less soluble *basic* salt, formed by adding a soluble cinchonate to a solution of acetate of copper.

*Cinchonate of red oxide of Mercury* is a colorless uncrystallizable salt. When its solution is evaporated, a reddish-yellow residue is obtained, which appears to be an altered salt.

*Cinchonate of Silver.* When a soluble cinchonate is mixed with nitrate of silver, the liquor deposits a black powder. But if a solution of cinchonic acid be saturated with carbonate of silver, under exclusion of



light, a neutral liquor may be obtained, which evaporated *in vacuo*, yields crystals eminently susceptible of the influence of light. They appear, according to Woskresensky's analysis, to be an acid salt  $= \text{AgO}, \text{HO}, 2[\text{C}_7 \text{H}_5 \text{O}_5]$

### III. STRYCHNIA. BRUCIA. STRYCHNIC ACID.

Strychnia was discovered, in 1818, by Pelletier and Caventou. (*Ann. Ch. et Ph.*, viii. 305, x. 142.) It is contained in many species of *Strychnos*, especially in *S. nux-vomica*, *S. ignatia*, and *S. colubrina*. They also subsequently detected it in the celebrated Javanese poison, called *Upastieute*. (*Ann. Ch. et Ph.*, xxvi. 44.)

Strychnia is associated in the former sources with *Brucia*, a distinct alkaloid, which was originally detected in the bark of the nux-vomica tree, an article which was known in the drug-trade under the name of *spurious angustura bark*; and as the genuine angustura bark was presumed to be the bark of a species of *brucia*, the terms *brucine* and *brucia*, though evidently derived from a perfectly distinct source, have been applied to the alkaloid, extracted together with strychnia, from the bark of the *S. nux-vomica*. *Brucia* was discovered by the above chemists in 1819. (*Ann. Ch. et Ph.*, xii. 118.) To them also we are indebted for our knowledge of the *strychnic*, or as they originally called it, *igasuric* acid, a term derived from the Malayan name of St. Ignatius' bean.

1. STRYCHNIA.  $\text{C}_{44} \text{H}_{24} \text{O}_4 \text{N}_2$ . Among the numerous processes which have been devised for the extraction of strychnia, the two following are the simplest: the first is suggested by Coriol, the second by Henry Jun. (*Journ. de Pharm.*, xi. 492; xvi. 752.)

Digest coarsely-powdered *nux-vomica* in repeated portions of cold water, till all soluble matters are extracted: carefully evaporate the infusions to the consistence of syrup, and precipitate by alcohol; wash the precipitate (which consists chiefly of gum) with alcohol, add the washings to the original portion, and evaporate the whole in a water-bath to the consistence of an extract: this consists almost entirely of *strychnate of strychnia*; dissolve it in cold water, which separates a little greasy matter; then heat the clear liquid, and add milk of lime so as to decompose the strychnate, and leave the lime in slight excess; drain, and dry the precipitate by pressure, and digest it in boiling alcohol, which takes up strychnia, brucia, and some coloring matter; these are obtained by evaporation, and may be separated by the action of weak alcohol, which dissolves the brucia and the coloring matter, and leaves strychnia; wash it with a little dilute alcohol, and dissolve it in strong boiling alcohol; this deposits it in crystals on cooling.

Henry's process is as follows: the rasped or powdered nux-vomica is digested in warm alcohol acidulated by sulphuric acid, as long as it dissolves anything; it is then pressed out, and powdered quicklime is added to the alcoholic liquors to saturate the acid, and precipitate the coloring matter: when this mixture has subsided, the clear part is poured off, the residue washed with alcohol, and these liquors filtered and distilled; they leave a brown alkaline residue, which is to be saturated by water slightly acidulated by sulphuric, hydrochloric, or

acetic acid; the neutral liquor is then filtered off, concentrated by evaporation if necessary, and when cold, precipitated by slight excess of ammonia; the precipitate is washed, and digested in warm dilute alcohol, to remove brucia; the remaining strychnia is then dissolved in boiling alcohol with a little animal charcoal, and filtered whilst hot; on cooling, the strychnia is deposited. (See DUMAS, v. 754, for an abstract of some other methods.)

The following is Merck's process, which, according to Liebig, is preferable to the others. The vomica nuts are boiled for 24 or 36 hours in a closed boiler, with water enough to cover them, acidulated by one-eighth of its weight of sulphuric acid; they are then bruised and beaten into a paste, and the liquor well expressed. Excess of caustic lime is then added to it, and the precipitate, having been pressed, is boiled in alcohol of sp. gr. .850, and filtered hot; strychnia and brucia are deposited together in a colored and impure state, and may be separated by cold alcohol, which dissolves the brucia; the remaining strychnia is then boiled in alcohol with a little animal charcoal, and the solution filtered boiling hot; on cooling the strychnia crystallizes. The same process is applicable to the Ignatius' beans.

When a solution of strychnia in common alcohol is left to slow evaporation, it yields the alkaloid in octohedra, or four-sided prisms terminated by pyramids; when rapidly crystallized it is granular. It is intensely bitter, and extremely poisonous, one-eighth of a grain being sufficient to kill a dog, and a quarter of a grain often producing a decided effect upon a healthy man. It produces, in larger doses, paroxysms of tetanus, and repeated convulsions, like those resulting from electric shocks. Injected in very small quantities into the veins, death very soon ensues, and in this way it is that the poisoned arrows of the Javanese produce their effect.

In the treatment of poisoning by nux vomica, or strychnia, emetics or the stomach-pump must be principally relied on, and unless these be employed early, the jaw may become spasmodically fixed, so as to render all means unavailing. In general, however, the spasms have intermissions, so as to admit of the application of remedies in the interval. The extract of the *Cannabis Indica* has been recommended in these cases as a sedative producing great relaxation of the muscular system, without dangerous effects even in large doses. (LEY. TAYLOR'S *Med. Jurisp.*, 266.) Infusion of galls, and strong tea, as containing *tannine*, have also been suggested as antidotes.

Strychnia is neither fusible nor volatile, but easily decomposed by heat; subjected to destructive distillation it affords the usual products of these compounds. It requires 7000 parts of cold, and 2500 of boiling water for solution: the intensity of its bitterness is such, that an aqueous solution which does not contain more than a forty-thousandth of its weight of strychnia, is sensibly bitter. It is soluble in common alcohol, especially at its boiling temperature, but absolute alcohol, and ether, scarcely dissolve it when quite free from acid. According to Duflos, alcohol of sp. gr. 0.870 dissolves 5 *per cent.* of strychnia; and, according to Merck, that of sp. gr. 0.934 dissolves one-24th at common temperatures. It is soluble in the acids, and forms soluble, colorless, and crystallizable salts. It is not soluble in the alkalis. When chlorine is



passed through a mixture of strychnia and water, it is dissolved, and the solution yields colorless crystals of hydrochlorate of strychnia by evaporation: boiled with iodine and water it is also dissolved. Fused with sulphur it evolves sulphuretted hydrogen. When pure it is only rendered yellow by nitric acid, but if it contain brucia, it is reddened by that acid.

“When a very small quantity of strychnia is triturated with a few drops of concentrated sulphuric acid containing one-hundredth of its weight of nitric acid, the strychnia disappears without any peculiar color, but if a minute quantity of peroxide of lead be added, a fine blue tint is developed which passes into violet and red, and after some hours, into yellow. This reaction is characteristic of strychnia.” (MARCHAND.)

Strychnia has been analyzed by Liebig, (*Chim. Org.*, ii. 558,) and by Regnault. (*Ann. Ch. et Ph.*, LXVIII. 125.) Liebig's analysis leads to the formula  $C_{44}H_{24}O_4N_2$ , which produces the equivalent 348. Regnault's formula is  $C_{42}H_{22}O_4N_2$ , which gives the equivalent 334. The analysis of such of the salts of strychnia as have been accurately examined lead to an intermediate equivalent; and as Regnault's experimental results are not inconsistent with Liebig's formula, the latter may probably be adopted without material error.

|                 |    |      |     |      |        | Liebig. |        | Regnault.  |
|-----------------|----|------|-----|------|--------|---------|--------|------------|
| Carbon .....    | 44 | .... | 264 | .... | 75·86  | ....    | 76·36  | .... 75·67 |
| Hydrogen .....  | 24 | .... | 24  | .... | 6·89   | ....    | 6·51   | .... 6·89  |
| Oxygen .....    | 4  | .... | 32  | .... | 9·19   | ....    | 9·09   | .... 9·09  |
| Nitrogen .....  | 2  | .... | 28  | .... | 8·04   | ....    | 8·04   | .... 8·35  |
| <hr/>           |    |      |     |      |        |         |        |            |
| Strychnia ..... | 1  |      | 348 |      | 100·00 |         | 100·00 | 100·00     |

*Salts of Strychnia.* This alkaloid perfectly neutralizes the acids, and forms soluble and very bitter and poisonous salts: they are mostly crystallizable. Their solutions are rendered turbid by aqueous chlorine; and chlorate of potassa and iodide of potassium form with them white precipitates; the caustic alkalis throw down a white precipitate of strychnia; with chloride of gold and chloride of platinum they give yellow precipitates: they are also precipitated by tincture of galls.

*Hydrochlorate of Strychnia.* <sup>+</sup>Str, H Cl, forms groups of acicular crystals, which became opaque in the air; it is very soluble in water, perfectly neutral, and when highly heated, is decomposed with the evolution of hydrochloric acid. After drying at  $265^{\circ}$ , this salt is anhydrous. It is best prepared by digesting strychnia to saturation in diluted hydrochloric acid, but it may also be obtained by exposing the alkaloid to the continued action of a current of hydrochloric gas, only in that case it is difficult to attain its perfect saturation. When a current of chlorine is passed through water holding strychnia in suspension, the alkaloid dissolves, probably in consequence of the formation of a chlorate and hydrochlorate. Chloride, cyanide, and nitrate of mercury occasion white flocculent precipitates in the solution of this hydrochlorate, which are crystalline when the liquor is much diluted. Perchloride of platinum throws down a yellow double salt containing 17·82 per cent. of platinum. (WINKLER. LIEBIG.) This salt consists of

|                                 |   |       |     |       |        |
|---------------------------------|---|-------|-----|-------|--------|
| Strychnia .....                 | 1 | ..... | 348 | ..... | 90·38  |
| Hydrochloric acid .....         | 1 | ..... | 37  | ..... | 9·62   |
| <hr/>                           |   |       |     |       |        |
| Hydrochlorate of strychnia..... | 1 |       | 385 |       | 100·00 |

*Chlorate of Strychnia*,  $\overset{+}{\text{Str}}, \text{Cl O}_5$ , obtained by saturating the dilute acid by strychnia, crystallizes in small short prisms; when heated, the solution becomes colored, and if concentrated, concretes on cooling into a crystalline mass.

*Hydriodate of Strychnia*,  $\overset{+}{\text{Str}}, \text{HI}$ , crystallizes in white flattened needles. It is so little soluble in cold water, that it is precipitated on adding a solution of iodide of potassium to a salt of strychnia. It appears to contain 1 atom of base and 1 of acid. (PELLETIER, *Ann. Ch. et Ph.*, LXiii. 172.)

*Iodate of Strychnia*.  $\overset{+}{\text{Str}}, \text{IO}_5$ . When strychnia is heated in a solution of iodic acid, it assumes a red color, and deposits on cooling acicular tufts of crystals which are superficially red, but become colorless when washed with cold water; they are very soluble in water, and suddenly decompose when heated. (PELLETIER.)

*Sulphate of Strychnia*.  $\overset{+}{\text{Str}}, \text{SO}_3, + 8\text{HO}$ . This salt crystallizes in small transparent cubes and rectangular prisms, which become opaque on exposure. Dried in the air it retains 8 atoms of water, 7 of which = 13·7 per cent. may be expelled by a heat of 212° without further decomposition: it then fuses, and solidifies on cooling. At a high temperature a portion of it volatilizes, and afterwards is decomposed. With excess of acid this salt forms a *bisulphate*, which crystallizes in needles. When strychnia is boiled in a solution of sulphate of copper, oxide of copper is thrown down, and on evaporating the filtered liquor, a green salt is obtained, which forms long green needles. Dried at 212°, sulphate of strychnia consists of

|                             |   |     |       |     |        |     |         |
|-----------------------------|---|-----|-------|-----|--------|-----|---------|
|                             |   |     |       |     |        |     | Liebig. |
| Strychnia .....             | 1 | ... | 348   | ... | 87·65  | ... | 85·6    |
| Sulphuric acid .....        | 1 | ... | 40    | ... | 10·07  | }   | 14·4    |
| Water .....                 | 1 | ... | 9     | ... | 2·28   |     |         |
| <hr/>                       |   |     | <hr/> |     | <hr/>  |     | <hr/>   |
| Sulphate of strychnia ..... | 1 |     | 397   |     | 100·00 |     | 100·0   |

*Nitrate of Strychnia*,  $\overset{+}{\text{Str}}, \text{NO}_5, \text{HO}$ , is obtained by saturating dilute nitric acid by strychnia; on evaporation it forms groups of nacreous needles, more soluble in hot than in cold water, sparingly soluble in alcohol, and insoluble in ether. When the dry salt is heated to a little above 212°, it becomes yellow, swells up, and explodes, leaving charcoal. An *acid nitrate* is produced by adding a little nitric acid to a hot solution of the neutral salt; it forms delicate needles, which redden when dried, and explode with ignition when heated. (LIEBIG. PELLETIER and CAVENTOU.)

*Phosphate of Strychnia* crystallizes in small prisms, when prepared by dissolving strychnia in aqueous phosphoric acid; their solution reddens blues. The composition of this salt has not been accurately determined.

*Carbonate of Strychnia*. The alkaline carbonates form a white pre-



precipitate in the solutions of the salts of strychnia. When carbonic acid is passed through strychnia diffused in water, the alkaloid gradually dissolves, and the liquor deposits small granular crystals, nearly insoluble in water.

*Hydrocyanate of Strychnia* is obtained by dissolving the alkaloid in hydrocyanic acid; it crystallizes on evaporation: its solution precipitates salts of iron blue.

*Hydrosulphocyanate of Strychnia* is formed by mixing an aqueous solution of a salt of strychnia with a solution of sulphocyanide of potassium; the mixture becomes turbid, and on agitation deposits the salt in white stellated crystals. Heated to  $160^{\circ}$  the salt dissolves, and forms silky needles on cooling.

*Tannate of Strychnia* is very sparingly soluble. Tannine forms no precipitate in solutions containing less than one part in 1000 of strychnia.

*Oxalate, Tartrate, and Acetate of Strychnia* are very soluble, and easily crystallize with excess of acid. The solution of the *acetate* is not precipitated by perchloride of mercury till hydrochloric acid is added, when a crystalline precipitate falls.

2. BRUCIA.  $C_{44}H_{25}O_7N_2 = \overset{+}{Br}u$ . The presence of this alkaloid in the usual sources of strychnia, and the method of separating them, have already been described. It is most abundantly procured from the bark of the *Strychnos nux-vomica*, commonly called *false angustura*. This bark is coarsely powdered, and having been previously digested in ether to free it from fatty matter, is treated by alcohol, the alcoholic solution evaporated, and the residue dissolved in water, saturated with oxalic acid, and evaporated to dryness. Alcohol, digested upon this residuum, dissolves coloring matter, and leaves pure *oxalate of brucia*, which may be decomposed by lime, and the brucia dissolved out by boiling alcohol, from which, by slow evaporation, it is obtained in crystals.

Brucia forms either prismatic or foliated crystals, according as it has been slowly or rapidly deposited: it is soluble in about 850 parts of cold, and in 500 of boiling water. Sometimes, on precipitating a salt of brucia by ammonia, the alkaloid separates in the form of an oil, which after a time concretes, if left in contact of water. The taste of brucia is strongly and permanently bitter; its poisonous action resembles that of strychnia, but is less potent; it is very soluble in alcohol, but insoluble in ether, and in the fat oils; it is sparingly soluble in essential oils. It forms soluble salts with the acids, which are mostly crystallizable; they are bitter, and are decomposed not only by the alkalis, but by morphia and strychnia, both of which precipitate the brucia. Brucia is reddened by nitric acid, and the color changes to violet on the addition of protochloride of tin; a drop of bromine added to the alcoholic solution of brucia renders it violet; by these characters it is distinguished from strychnia and from the other alkaloids. Sulphuric acid first reddens it, and then turns it yellow and green.

*Anhydrous brucia* consists of

|                |    |      |     |      |        | Liebig. | Regnault. |      |        |
|----------------|----|------|-----|------|--------|---------|-----------|------|--------|
| Carbon .....   | 44 | .... | 264 | .... | 70·78  | ....    | 71·11     | .... | 70·39  |
| Hydrogen ..... | 25 | .... | 25  | .... | 6·70   | ....    | 6·60      | .... | 6·50   |
| Oxygen.....    | 7  | .... | 56  | .... | 15·01  | ....    | 14·80     | .... | 16·03  |
| Nitrogen ..... | 2  | .... | 28  | .... | 7·51   | ....    | 7·49      | .... | 7·08   |
| <hr/>          |    |      |     |      |        |         |           |      |        |
| Brucia .....   | 1  |      | 373 |      | 100·00 |         | 100·00    |      | 100·00 |

Crystallized brucia contains 8 atoms of water (REGNAULT, *Ann. Ch. et Ph.*, LXVIII. 129): it is therefore represented by the equivalent  $373 + 72 = 445$ , and consists of

|                           |   |      |     |      |        |
|---------------------------|---|------|-----|------|--------|
| Anhydrous brucia .....    | 1 | .... | 373 | .... | 83·82  |
| Water .....               | 8 | .... | 72  | .... | 16·18  |
| <hr/>                     |   |      |     |      |        |
| Crystallized brucia ..... | 1 |      | 445 |      | 100·00 |

*Hydrochlorate of Brucia.*  $\text{Bru, HCl}$ . According to Liebig, 100 parts of brucia absorb about 13·06 of hydrochloric gas; but according to Regnault only 9·3. The salt crystallizes in acicular prisms, and is very soluble in water. It forms a yellow pulverulent double salt with bichloride of platinum, containing 16·6 *per cent.* of platinum.

*Chlorate of Brucia.* When dilute chloric acid is heated with brucia, it assumes a red tint; on cooling, transparent rhomboids are deposited, which are colorless after a second solution and crystallization.

*Hydriodate of Brucia* forms short rectangular prisms sparingly soluble in cold water, but very soluble in boiling water, and in alcohol. With iodic acid this salt gives a brown precipitate containing 6 atoms of iodine to 1 of brucia. (LIEBIG.)

*Sulphate of Brucia*,  $\text{Bru, SO}_3, + 8\text{HO}$ , forms slender needles very soluble in water, and slightly so in alcohol. It effloresces in the air.

*Nitrate of Brucia*,  $\text{Bru, NO}_5, + 5\text{HO}$ , forms a gum-like salt. The *acid nitrate* crystallizes in four-sided prisms with dihedral summits. It first reddens, and then blackens and deflagrates, when heated.

*Phosphate of Brucia*, with excess of acid, crystallizes in rectangular tables, with bevelled edges: it is efflorescent, and very soluble.

*Oxalate of Brucia* forms long needles, especially in the presence of excess of acid. It is soluble in alcohol.

*Acetate of Brucia* is very soluble, and has not been crystallized.

3. STRYCHNIC ACID. *Ignasuric Acid.* This acid was obtained by Pelletier and Caventou as follows:—Powdered Ignatius' bean, or nuxvomica, was first digested in ether, and all soluble matters being removed, it was next treated by alcohol; the alcoholic solutions were evaporated, water added to the residue, and filtered; the filtered liquor was then digested with pure magnesia; an insoluble *strychnate of magnesia* was thus formed, which, washed with cold water and dried, was digested in alcohol to abstract free strychnia; the strychnate of magnesia was then dissolved in boiling water, rapidly filtered, and mixed, whilst hot, (for the salt is not soluble in cold water,) with acetate of lead: the resulting *strychnate of lead* was then decomposed by sulphuretted hydrogen, and the sulphuret of lead being filtered off, or allowed to settle, the solution



was evaporated; it yielded a brown liquid, which deposited hard granular crystals of *strychnic acid*. Neither the equivalent nor the ultimate composition of this acid have been satisfactorily determined.

*Strychnates.* The *strychnates* of *ammonia*, *potassa*, and of *soda*, are very soluble both in water and in alcohol: when the aqueous solution of *strychnate of baryta* is evaporated, it yields spongy vegetations. The salts of *iron*, *mercury*, and *silver*, are not affected by neutral *strychnate* of *ammonia*, but it renders the solutions of *copper* green, and, after some time, a bright-green precipitate, scarcely soluble in water, falls: Pelletier and Caventou regard this character as distinctive of the *strychnic acid*. (*Ann. Ch. et Ph.*, x. 167.)

#### IV. VERATRIA. SABADILLIA. JERVIA. CEVADIC ACID. COLCHICIA.

VERATRIA.  $C_{34}H_{22}O_6N = \overset{+}{\text{Ver}}$ . This alkaloid was discovered, in 1819, by Pelletier and Caventou (*Ann. Ch. et Ph.*, xiv. 69), and, about the same time, by Meisner, in Germany. (*Schweigger's Journ.*, xxv. 377.) It is contained in the seeds of the *Veratrum sabadilla*, and in the roots of the *Veratrum album*, or *white hellebore*, united with gallic acid. It is most readily procured from the seeds of the *sabadilla* or *cebadilla*, which are first digested in ether, to remove oily matter, then boiled in alcohol, and the solution suffered to cool; it is then filtered, evaporated to dryness, and the residue digested in water: which, being partly evaporated, deposits a yellow matter, to be separated by filtration. The clear solution is now mixed with acetate of lead, which gives a precipitate, to be removed by filtering; and the filtered liquor (its lead having been separated by sulphuretted hydrogen, and heated) is now boiled with magnesia; the precipitate thus produced is digested in boiling alcohol, from which the veratria is deposited in a pulverulent form, on evaporation. If not at first white, it may be rendered so by a second solution, and by the aid of animal carbon. As thus procured, and constituting what is termed *commercial veratria*, it is not crystallizable; it has a pungent, but not a bitter taste, and powerfully irritates the nostrils. A very small dose produces nausea and vomiting. It fuses at a temperature of  $122^{\circ}$ , and concretes, on cooling, into a translucent yellow mass. Boiling water does not take up more than a thousandth part of its weight, but it is readily soluble in alcohol, and somewhat less so in ether. But in this state, veratria, according to Couerbe (*Ann. Ch. et Ph.*, lii. 352), is still blended with other principles, two of which are abstracted by boiling water: of these, one is crystallizable, and termed *sabadillia*; the other is deposited on the evaporation of the mother-liquor in the form of viscid drops of a reddish color and acrid taste: he has termed it *resinigomme de sabadilline*. The alkaline residue of the veratria remaining after this treatment, is digested in successive portions of ether, and when these ethereal solutions are spontaneously evaporated, they deposit a white viscid matter, which is now *pure veratria*: the matter which resists the action of ether is called by Couerbe, *veratrin*. According to Pereira, (*Mat. Med.*, 961,) the components of *commercial* or *medicinal veratria*, as obtained by the process of the *London Pharmacopœia*, may be separated from each other by the successive action of water, ether, and alcohol, as shown by the following table:

|                        |   |                              |   |   |  |
|------------------------|---|------------------------------|---|---|--|
| Commercial<br>Veratria | { | yields to boiling water .... | { | 1 | <i>Sabadillia</i> , which crystallizes on cooling.                       |
|                        |   | insoluble in boiling water   |   | 2 | <i>Resin of veratria</i> ( <i>veratrin</i> ), left in the cold solution. |
|                        |   |                              |   | 3 | <i>Veratria</i> , soluble in ether.                                      |
|                        |   |                              |   | 4 | <i>Gum resin</i> , insoluble in ether, but soluble in alcohol.           |

Pure veratria consists, according to Couerbe, of

|                |    |      |     |      |        | Couerbe.    |
|----------------|----|------|-----|------|--------|-------------|
| Carbon.....    | 34 | .... | 204 | .... | 70.83  | .... 70.786 |
| Hydrogen ..... | 22 | .... | 22  | .... | 7.64   | .... 7.636  |
| Oxygen .....   | 6  | .... | 48  | .... | 16.67  | .... 16.368 |
| Nitrogen ..... | 1  | .... | 14  | .... | 4.86   | .... 5.210  |
| <hr/>          |    |      |     |      |        |             |
| Veratria ..... | 1  |      | 288 |      | 100.00 | 100.000     |

*Salts of Veratria.* Veratria forms compounds with the acids, which are very difficult of crystallization. Couerbe succeeded in obtaining a crystallizable *sulphate of veratria*, from the analysis of which he established the equivalent of veratria as above. The *hydrochlorate of veratria* is also a crystallizable salt.

*Sabadillia*, or *Sabadillina*, was obtained by Couerbe, as above described, and regarded by him as a distinct alkaloid. He represents it as = C<sub>20</sub> H<sub>13</sub> O<sub>5</sub> N. According to Simon, (*Pharm. Central Blatt*, 1839, p. 235,) it is merely a compound of soda, veratria, and a resin. The same chemist has announced the presence of two new bases (in addition to veratria,) contained in the rhizome of veratrum, namely, *Jervia* (or *Jervine*), so called from *Jerva*, the Spanish name of a poison obtained from the root of *white hellebore*, and *Barytina*, a substance, which like baryta is precipitated from its soluble combinations by sulphuric acid and the sulphates. The formula ascribed to jervia is C<sub>60</sub> H<sub>45</sub> O<sub>3</sub> N<sub>2</sub>: it is obtained by digesting the alcoholic extract of the root in dilute hydrochloric acid, filtering, and precipitating the filtered liquor by carbonate of soda. The precipitate is dissolved in alcohol, decolorized by charcoal, and the alcohol distilled off so as to leave a crystalline magma, from which the greater part of the uncrystallized veratria may be pressed out; on similarly treating the product several times, by alcohol and pressure, the jervia remains nearly pure. The expressed liquors still contain a considerable portion of jervia, which may be separated by evaporating them to dryness, and digesting the residue in dilute sulphuric acid, which forms a very soluble sulphate of veratria, whilst the difficultly soluble sulphate of jervia remains.

According to Will, jervia is white, crystalline, and fusible; its compounds with hydrochloric, nitric, and sulphuric acid are little soluble in water and in acids; the *acetate of jervia* is, however, very soluble, and is precipitated by ammonia and by the three mineral acids; it gives a yellow precipitate with bichloride of platinum, containing about 14.5 per cent. of platinum. (LIEBIG.)

VERATRIC ACID. *Sabadillic Acid.* C<sub>18</sub> H<sub>9</sub> O<sub>7</sub> + HO. This acid was discovered by Merck in the seeds of *Veratrum sabadilla*. The bruised seeds are digested in alcohol acidulated by sulphuric acid; this acid is afterwards abstracted by lime, and the *veratrate of lime* remains dissolved. The alcohol is then distilled off, and the remaining aqueous



liquor, after it has deposited veratria, retains the salt of lime, which is decomposed by warm dilute sulphuric acid, and the filtered liquor then deposits crystals of veratric acid. These crystals are then redissolved in alcohol to free them from adhering sulphate of lime, the solution is treated by animal charcoal, filtered, and set aside for spontaneous evaporation, when four-sided acicular prisms are deposited, having, according to Schrötter, the above formula.

The *veratrates* of the *alkalis* are crystallizable and soluble in water and in alcohol. The *veratrates* of *lead* and of *silver* are difficultly soluble, and are apparently undecomposed by sulphuric and nitric acid.

CEVADIC ACID is obtained from the *oil* of the *sabadilla* seed, which is abstracted by ether, saponified by potassa, and the potassa-soap decomposed by a salt of baryta. The barytic compound is then decomposed by distillation with syrupy phosphoric acid, and the cevadic acid sublimes in white nacreous needles. This acid has the odor of butyric acid; it fuses at  $70^{\circ}$ , and is soluble in alcohol and in ether. (PELLETIER and CAVENTOU, *Journ. de Pharm.*, vi. 457.)

COLCHICIA. *Colchicine*. This substance, originally confounded with veratria, has been shown by Geiger and Hesse, to exist in the *Colchicum autumnale*, as a distinct alkaloid, but it has not been analysed, nor has its atomic weight been determined. It exists in the bulb and flowers gathered in July, but is best obtained from the pulverized seed, which is digested in alcohol acidulated by sulphuric acid; lime is then added to the liquor, which is filtered, saturated by sulphuric acid, and the alcohol expelled by distillation. The remaining concentrated aqueous solution having been decomposed by excess of carbonate of potassa, the precipitate is dried and digested in absolute alcohol. This alcoholic solution of the alkaloid is then decolorized by animal charcoal, filtered, and gently evaporated; the product is afterwards purified by repeated crystallizations.

Colchicia crystallizes in colorless needles, bitter, and very poisonous; purging and vomiting in very small doses; it is slightly alkaline, and easily fusible. It is rendered deep blue by concentrated nitric acid, becoming afterwards olive-colored and yellow; sulphuric acid renders it brown, and not blue, by which it is distinguished from veratria. It is soluble in water, alcohol, and ether, and its aqueous solution is precipitated by tincture of iodine, by solution of platinum, and by infusion of galls. It neutralizes the acids, and forms salts which are mostly crystallizable, permanent in the air, and very bitter and acrid. They are soluble in water and in alcohol, and their aqueous solutions are acted upon by reagents similarly to colchicia. When not too dilute, the alkalis precipitate the alkaloid.

#### V. ATROPIA. HYOSCYAMIA. SOLANIA. DATURIA. PICROTOXIA.

ATROPIA. The existence of an alkaloid in the *Atropa belladonna*, or *deadly nightshade*, was first shown by Brandes, in 1819, (*Schweigger's Journ.*, xxviii.,) and the process for obtaining it was afterwards improved by Mein (*Journ. de Pharm.*, xx. 87), in consequence of Runge's discovery of the destructibility of some of these bases by the fixed alkalis.

The following is the process:—80 parts of the powdered root of *belladonna*, from plants two or three years old, are digested in 60 parts of alcohol (0·830) for several days; the alcohol is then pressed out, and the residue treated by fresh alcohol. The tinctures are mixed, filtered, and 1 part of slaked lime is added, the whole being left for 24 hours and then filtered. Sulphuric acid is then dropped in in slight excess, and the resulting sulphate of lime separated by filtration. Distil off half the filtered liquor, add 6 parts of water to the residue, and drive off the remaining alcohol by heat: concentrate carefully to one-third its bulk, and when cold, drop into the liquor a strong solution of carbonate of potassa as long as it precipitates the atropia, which falls in a gelatinous form; it may be freed from mother-water by pressure in bibulous paper, dried, and dissolved in 5 parts of alcohol; filter, and dilute with 6 of water; evaporate the alcohol, and set the remaining solution aside, when the atropia forms yellowish crystals: 1000 parts of the root yield about 3 of the alkaloid. It may be similarly obtained from an extract of the leaves.

Atropia crystallizes in silky prisms: it is soluble in anhydrous alcohol and in ether, and in about 500 parts of cold water; this solution is nauseously bitter, and when dropped into the eye, dilates the pupil. When obtained by the evaporation of its alcoholic solution, it sometimes forms a glass-like residue. It is very alkaline; it fuses at  $212^{\circ}$ , and at a somewhat higher temperature is partly decomposed and partly volatilized. It produces a pale yellow solution in nitric acid, which, when boiled, acquires an orange color, and afterwards becomes colorless, evolving nitrous fumes. With sulphuric acid it forms a colorless solution, which blackens when heated.

Atropia forms definite compounds with the acids; the sulphate and acetate are more crystallizable than the hydrochlorate or nitrate: the salts are decomposed, and the atropia thrown down by potassa and ammonia, by infusion of galls, and by chlorides of gold and platinum, with which it forms compounds gradually crystallizing, and probably composed of hydrochlorate of atropia combined with the metallic chloride.

When atropia is heated with potassa it is easily decomposed, and abundance of ammonia is evolved. The facility with which this alkaloid is thus destroyed, renders the use of caustic alkalis in its preparation inadmissible. According to Liebig, the formula of atropia is  $C_{34}H_{23}O_6N$ , which gives the equivalent 289.

|                |    |      |     |      |        | Liebig.    |
|----------------|----|------|-----|------|--------|------------|
| Carbon .....   | 34 | .... | 204 | .... | 70·58  | .... 70·98 |
| Hydrogen ..... | 23 | .... | 23  | .... | 7·96   | .... 7·83  |
| Oxygen .....   | 6  | .... | 48  | .... | 16·61  | .... 16·36 |
| Nitrogen ..... | 1  | .... | 14  | .... | 4·85   | .... 4·83  |
| Atropia .....  | 1  |      | 289 |      | 100·00 | 100·00     |

HYOSCYAMIA. This alkaloid was obtained by Brandes from the seeds of the *Hyoscyamus niger*; an alcoholic solution or tincture of which was mixed with a small quantity of lime, and the precipitate digested in dilute sulphuric acid; the solution, containing sulphate of hyoscyamia, was then decomposed by the addition of powdered carbonate of soda; the hyoscyamia was thus precipitated, quickly removed from the



solution, and dried by pressure in blotting-paper; it was then dissolved in absolute alcohol, filtered through animal charcoal, and the solution evaporated, a little water being added towards the end of the process.

Another process has been suggested by Geiger and Hesse for the extraction of hyoscyamia, but it appears to have failed in the hands of Chevallier and others, (*Journ. de Pharm.*, xxi. 134,) and as yet the alkaloid has not been analyzed, nor has its equivalent been determined.

Hyoscyamia is described as forming silky crystals, difficultly soluble in water, of an acrid and nauseous taste, highly poisonous, and, when applied to the eye, producing a dilated pupil. It is easily decomposed, with the evolution of ammonia, by the fixed alkalis. It is very soluble in alcohol and ether: its salts are said to be neutral and crystallizable. (GEIGER and HESSE, *Journ. de Pharm.*, xx. 92.)

SOLANIA.  $C_{84}H_{68}O_{28}N$ . This alkaloid was discovered in 1821 by Desfosses of Besançon, in the berries of the *Solanum nigrum*, and in the leaves of the *Solanum dulcamara*. (*Journ. de Pharm.*, vi. and vii.) The filtered juice of the ripe berries was saturated by solution of ammonia, which threw down a gray powder: this was dissolved in boiling alcohol, filtered through animal charcoal, and evaporated, when the solania was deposited.

Otto and Henry have extracted solania from the fruit, leaves, and stem of the potato (*Solanum tuberosum*), and especially from the germs of old potatoes growing in cellars. A decoction of the germs in dilute sulphuric acid is decomposed at its boiling-point by ammonia, and the precipitate, after having been washed with ammonia, is dissolved in boiling alcohol, which deposits crystalline solania on cooling. Sometimes the alcoholic solution gelatinizes, and on desiccation yields a horn-like product which cannot be made to crystallize; this appears to depend upon the presence of some foreign matter. (KEELING.) Otto decomposes the acidulated decoction of the white potato germs by acetate of lead, filters the mixture, and adds excess of milk of lime to the filtered liquor, washes the precipitate, digests it in alcohol, evaporates, and recrystallizes. (*Journ. de Pharm.*, xx. 96.) Wackenroder obtained it from potato-apples. (*Chem. Gaz.*, April, 1843.)

Solania is generally in the form of a crystalline powder of a nauseous, bitterish, and acrid taste. A grain of it dissolved in dilute sulphuric acid killed a rabbit in six hours; four grains of the sulphate caused in an hour paralysis of the hind legs, and in eight hours, death. It does not dilate the pupils like the other alkaloids of the *Solanaceæ*. It has a slight alkaline reaction, and is very sparingly soluble in water. It cannot be fused without decomposition. The salts of solania are mostly uncrystallizable; they have been chiefly examined by Otto, and by Payen and Chevallier. (*Journ. de Chim. Med.*, i. 517.) Baumann has described several of the salts of solania with the organic acids.

Solania has hitherto only been analyzed by Blanchet, with the following results, which, if correct, render it remarkable for its high equivalent and its small proportion of nitrogen; the solania was carefully dried.

|                        |    |      |     |      |        |            |
|------------------------|----|------|-----|------|--------|------------|
|                        |    |      |     |      |        | Blanchet.  |
| Carbon .....           | 84 | .... | 504 | .... | 62.22  | .... 62.11 |
| Hydrogen .....         | 68 | .... | 68  | .... | 8.40   | .... 8.92  |
| Oxygen .....           | 28 | .... | 224 | .... | 27.65  | .... 27.33 |
| Nitrogen .....         | 1  | .... | 14  | .... | 1.73   | .... 1.64  |
| <hr/>                  |    |      |     |      |        | <hr/>      |
| Anhydrous solania .... | 1  |      | 810 |      | 100.00 | 100.00     |

DATURIA. Daturia was discovered by Brandes in the seeds of the *Datura stramonium*. Geiger and Hesse obtained it by the same process as that for procuring hyoscyamia. (*Journ. de Pharm.*, vi. and xx.) The following process is given by Simes, for its extraction. A pound of stramony seeds, in fine powder, was boiled for an hour in 3 quarts of weak alcohol; to the liquor, filtered whilst hot, half an ounce of magnesia was added, and the mixture shaken from time to time for 24 hours; the precipitate was then collected, boiled for some minutes with 12 ounces of alcohol, and filtered through animal charcoal; this alcoholic solution was then evaporated to half its bulk, and set aside for 24 hours, when it was found to have deposited globules of oil and crystals of colorless daturia; this deposition continued during the spontaneous evaporation of the liquor, when the daturia was collected, dissolved in acidulated water, filtered through charcoal, precipitated by magnesia, again dissolved by alcohol, and obtained in a pure form. Daturia crystallizes in colorless quadrangular prisms, of a bitter and acrid taste, and is very poisonous; applied to the eye, the pupil is durably dilated. Its aqueous solution is decidedly alkaline. It is soluble in about 280 parts of cold, and 72 of boiling water, and readily soluble in alcohol. Daturia has not been analyzed, nor has its equivalent been determined.

The salts of daturia are generally soluble, crystallizable, and permanent in the air; they are decomposed by the alkalis, and daturia falls in white flocculi. Dumas, adverting to the analogy that subsists between daturia, atropia, and hyoscyamia, suggests the possibility of their identity: their ready decomposition by the fixed alkalis approximates them to the amides; and it seems probable that a more accurate knowledge of their ultimate composition may throw light upon the subject of the alkaloids in general.

PICROTOXIA. This name has been given to a poisonous bitter substance, discovered by Boullay in 1819, (*Ann. de Chimie*, lxxx. 209,) in the berries of the *Menispermum cocculus*, or *Cocculus indicus*. It may be obtained by the following process:—add acetate of lead to a decoction of the berries, as long as any precipitate falls; filter, evaporate, and digest the extract in highly rectified alcohol; evaporate to dryness, and agitate the remaining matter with a little water; the picrotoxia remains in the form of a white residue of a bitter taste.

Picrotoxia is difficultly soluble in water. Alcohol, of the specific gravity of .810, dissolves one-third its weight. It is soluble in weak solutions of the pure alkalis. Picrotoxia was originally described by Boullay as a salifiable base, and as united in the seeds to a peculiar acid, which was termed *menispermic acid*. Casaseca has shown that this acid is a mixture of malic and sulphuric acids, and that picrotoxia has no alkaline reaction, and does not neutralize the acids; but it certainly



appears to form definite compounds with the acids, some of which are crystallizable. Its ultimate composition has not been accurately ascertained; but, according to Opperman, it does not contain nitrogen, but consists of 61·5 carbon, 6·1 hydrogen, and 32·4 oxygen *per cent*.

*Menispermia* and *Paramenispermia*. These substances were discovered in 1834 by Pelletier and Couerbe. (*Ann. Ch. et Ph.*, Liv. 181.) The alcoholic extract of the cocculus is boiled in water, and the liquor filtered whilst hot; it is then slightly acidulated, and on cooling deposits picrotoxia. The portion which is insoluble in boiling water is then digested in acidulated water and precipitated by an alkali. The granular precipitate which falls is then treated by alcohol, which separates a yellow coloring matter, and lastly dissolved in ether, from which the *menispermia* separates in crystals. The ether retains a viscous matter, which is soluble in absolute alcohol, and this solution evaporated at 112°, yields crystals of *paramenispermia*.

Menispermia is white, fusible at 250°, insoluble in water, but soluble in alcohol and ether; it dissolves in dilute acids, and forms salts; its *sulphate* crystallizes in prisms, fusible at 330°. The formula assigned to menispermia by Pelletier and Couerbe is C<sub>18</sub> H<sub>12</sub> O<sub>2</sub> N.

|                   |    |      |     |      |        | Pelletier<br>and Couerbe. |
|-------------------|----|------|-----|------|--------|---------------------------|
| Carbon .....      | 18 | .... | 108 | .... | 72·00  | .... 71·89                |
| Hydrogen .....    | 12 | .... | 12  | .... | 8·00   | .... 8·01                 |
| Oxygen .....      | 2  | .... | 16  | .... | 10·66  | .... 10·53                |
| Nitrogen .....    | 1  | .... | 14  | .... | 9·34   | .... 9·57                 |
| <hr/>             |    |      |     |      |        | <hr/>                     |
| Menispermia ..... | 1  |      | 150 |      | 100·00 | 100·00                    |

Paramenispermia is an isomeric compound; it fuses at 482°, and rises in white vapor, which condenses upon cold substances; it is insoluble in water, sparingly soluble in ether, and very soluble in boiling alcohol: it is also soluble in weak acids, but it does not neutralize them, nor does it form salts.

VI. NICOTINA. CONIA.

NICOTINA. C<sub>10</sub> H<sub>8</sub> N. Vauquelin in 1809 pointed out the presence of an acid alkaline oil in tobacco, to which its poisonous powers were referred. (*Ann. de Chim.*, LXXI. 137.) The products of the plant were afterwards examined by Hermbstaedt, (*Schweigger's Journ.*, xxxi. 441,) and by Posselt and Reimann. (*Mag. Pharm.*, xxiv. 139.) The latter chemists discovered *nicotina*. It is obtained by boiling dry tobacco-leaves in water acidulated by sulphuric acid, and evaporating the decoction; the residue, digested in alcohol, yields a solution of sulphate of nicotina, which, concentrated and distilled with quicklime, furnishes a solution of ammonia and nicotina. Ether abstracts nicotina from this solution, and when a sufficiently concentrated ethereal solution has been thus obtained, it must be deprived of water by agitation with chloride of calcium, decanted, and distilled; the nicotina remains in the retort.

When fresh tobacco-leaves are used, the juice is expressed, clarified, and concentrated; slaked lime is then added to it, and it is carefully distilled; the nicotina may be abstracted from the distillate by means of ether. Nicotina and ammonia may be separated by saturating them by

sulphuric acid, evaporating to dryness, and digesting the residue in absolute alcohol, which dissolves the sulphate of nicotina and leaves sulphate of ammonia: the former may be decomposed by baryta.

Pure nicotina is a colorless, limpid, oleaginous liquid, having a slight odor of tobacco, but when it is not free from ammonia this odor is very intense. At a temperature below  $475^{\circ}$  it may be slowly distilled, but at that temperature it is decomposed; its sp. gr. is 1.048. (O. HENRY and BOUTRON-CHARLARD, *Journ. de Pharm.*, xxii. 692.) It is alkaline to test papers; it is very inflammable, and burns with a smoky flame. When dissolved in water, caustic potassa separates it in the form of oily drops. Ether abstracts it from its aqueous solution. It dissolves in all proportions in alcohol and in oils. It is decomposed when heated with hydrate of potassa. Exposed to air it becomes brown and resinous, and it is decomposed by chlorine, iodine, and nitric acid. It is eminently poisonous, but does not occasion dilatation of the pupil; half a drop killed a rabbit; one drop was fatal to a dog; a tenth of a grain applied to the eye of a cat, occasioned violent convulsions and paralysis of the posterior extremities, which lasted for an hour. Nicotina neutralizes the acids and forms difficultly crystallizable salts, which are very soluble in water and in alcohol. When it is slightly supersaturated by hydrochloric acid, nicotina gives no precipitate with bichloride of platinum, but the mixture, after some hours, deposits acicular crystals. If the nicotina contain ammonia, it occasions an immediate precipitate. The solution of nicotina produces a white precipitate with corrosive sublimate.

Nicotina has been analyzed by Ortigosa and Barral with the following results; (LIEBIG, *Chim. Org.*, ii. 555.)

|                |    |      |    |      | Ortigosa<br>and Barral. |            |
|----------------|----|------|----|------|-------------------------|------------|
| Carbon.....    | 10 | .... | 60 | .... | 73.17                   | .... 73.26 |
| Hydrogen ..... | 8  | .... | 8  | .... | 9.75                    | .... 9.65  |
| Nitrogen ..... | 1  | .... | 14 | .... | 17.08                   | .... 17.09 |
| <hr/>          |    |      |    |      |                         |            |
| Nicotina ..... | 1  |      | 82 |      | 100.00                  | 100.00     |

CONIA.  $C_{16}H_{16}N$ . *Cicuta*. It appears from the experiments which have been made upon hemlock, that its active principle resides in a volatile and uncrystallizable alkaloid; its properties have been investigated by Geiger (*Journal für Pharmacie*, xxv.), by Boutron-Charlard and O. Henry (*Ann. Ch. et Ph.*, lxi. 337), and by Dr. Christison (*Edin. Phil. Trans.*, 1836, p. 383), whose paper upon the subject includes some valuable physiological experiments. When the seeds or leaves of hemlock are distilled with water, the fluid which passes over has the odor of the plant, but is not poisonous; but when caustic lime or potassa are previously added to the green seeds or leaves, and distilled with water at as low a temperature as possible, the liquid which then passes over is both alkaline and poisonous: when 10 or 12 lbs. of the seeds are worked at once, an oily matter comes over at first, which is nearly pure conia, but the greater part of the alkaloid is dissolved in the distilled water; if this be redistilled, it loses a little of its strength; but if previously neutralized by an acid, such as the sulphuric, the poisonous principle becomes fixed, and water alone distils over. The residue consists of sulphate of conia, sulphate of ammonia, and resin, the latter being produced by the decom-



position of part of the conia. To obtain the conia, the above residue is digested in a mixture of 2 parts of alcohol and 1 of ether, which leaves the sulphate of ammonia; and then, the alcohol and ether being carefully distilled off, the remaining sulphate of conia is heated gently with a little water and caustic potassa, when there is obtained in the receiver a watery solution of conia in the lower part, and floating on this, a layer of nearly pure hydrate of conia, containing a trace of ammonia; the water may be abstracted by chloride of calcium, and the ammonia by exposure *in vacuo*.

Conia, thus obtained, has the appearance of a colorless volatile oil, lighter than water, of a powerful diffusible odor, somewhat like that of hemlock, and intensely acrid to the taste. It has a strong alkaline action on reddened litmus and on turmeric. It is readily soluble in diluted acids, which it neutralizes, but its salts have not been crystallized. It is sparingly soluble in water, and combines with about a fourth of its weight of water to form a *hydrate*. This hydrate, and its aqueous solution, become opaque when slightly heated, and again transparent on cooling. Exposed to air, conia soon becomes brown, and is slowly resolved into a resinous matter, with the disengagement of ammonia; heat accelerates this change, so that it requires to be carefully excluded from air. It readily distils over with water at  $212^{\circ}$ , but its boiling-point is  $370^{\circ}$ , and it cannot be distilled, either alone or with water, without a considerable part being decomposed.

Christison observes that conia is most abundantly obtained from the seeds, fully developed, but still green; even from these, however, the quantity is small; from 40 pounds he obtained two ounces and a half of hydrated conia; but it probably exists in the plant in larger proportion, for much of it is always decomposed in the processes of separation, as is indicated by the evolution of ammonia.

Geiger observed that the *dried* leaves of hemlock contain no conia, and that it is not to be found in many specimens of the extract, hence the discrepancies respecting its efficacy. According to Christison the extract becomes feeble or inert in two ways; either by having been overheated towards the end of the process, or by long keeping, exposed to air; in both cases ammonia is formed, and extracts well prepared at first, become inert in a few years. To ascertain if conia be present, the extract, or other preparation, may be triturated with solution of potassa, upon which the odor of conia, if present, is strikingly perceptible. The alcoholic extract of the ripe seeds appears to be most efficacious. Probably some salt of conia will prove to be the most effective and convenient form for its medical use.

Conia is a deadly poison to every order of animals; it first palsies the voluntary muscles, then the respiratory muscles and the diaphragm, thus ending in death by asphyxia. The heart continues to act after other signs of life are extinct. Few poisons equal it in subtilty or swiftness; a drop put into the eye of a rabbit, killed it in nine minutes; three drops, in the same way, killed a strong cat in a minute and a half; two grains of conia, neutralized with hydrochloric acid, and injected into the femoral vein of a young dog, produced almost instant death: "in two seconds, or three at furthest, and without the slightest warning struggle, respiration had ceased, and with it all external signs of life."

Conia is probably combined in the recent plant with some vegetable acid, the nature of which has not, however, been ascertained. The analysis of conia by Ortigosa, as quoted by Liebig, shows that like nicotina, it contains no oxygen; indeed its composition is remarkable, as the formula shows, being

|                |    |      |     |      |        |      |                    |
|----------------|----|------|-----|------|--------|------|--------------------|
| Carbon.....    | 16 | .... | 96  | .... | 76.19  | .... | Ortigosa.<br>76.45 |
| Hydrogen ..... | 16 | .... | 16  | .... | 12.69  | .... | 12.48              |
| Nitrogen ..... | 1  | .... | 14  | .... | 11.12  | .... | 11.07              |
| <hr/>          |    |      |     |      |        |      |                    |
| Conia .....    | 1  |      | 126 |      | 100.00 |      | 100.00             |

VII. ACONITA. DIGITALIA. DELPHIA. CORYDALIA. CHELERYTHRIA.  
CHELIDONIA. SANGUINARIA. EMETINA.

ACONITA. This is an extremely poisonous and active alkaloid, extracted from the aconite; it is probably contained in several species of that plant. The following directions for its preparation are given in the *London Pharmacopæia*: "Take of the root of aconite, dried and bruised, 2 pounds; rectified spirit, 3 gallons; diluted sulphuric acid, solution of ammonia, purified animal charcoal, of each as much as may be sufficient. Boil the aconite for one hour with a gallon of the spirit, in a retort to which a receiver is adapted; pour off the liquor, and again boil the residue with another gallon of the spirit, and with that which had distilled over, and also pour off the liquor. Let the same be done for a third time. Then press out the aconite, and having mixed all the liquors, strain them, and distil off the spirit. Evaporate what remains to the proper consistency of an extract. Dissolve this in water, and strain. Evaporate the liquor by a gentle heat, till it acquires the consistency of syrup. To this, add a sufficient quantity of dilute sulphuric acid, mixed with water, to dissolve the aconitina. Then drop in the solution of ammonia, and dissolve the precipitated aconitina in dilute sulphuric acid and water, mixed as before. Afterwards mix the animal charcoal, occasionally shaking the mixture during a quarter of an hour. Lastly, strain, and again drop in solution of ammonia to precipitate the aconitina, which is to be washed and dried."

The following are the properties of pure aconita as given by Pereira; "It is a white odorless solid, either dull and amorphous, or somewhat sparkling, and apparently crystalline. As it is usually described as being crystallizable, I have carefully examined a supposed crystalline mass with the microscope, but I could not detect distinct crystals. The fragments appeared like thin plates of chlorate of potash, and though they varied greatly in shape, the triangular form seemed predominant. Heated in a tube, aconita readily fuses, and forms a pale amber-colored liquid; and at a higher temperature decomposes. It is not volatile. Heated on platinum, or over a spirit-lamp, it is speedily and entirely dissipated. It is soluble in alcohol, ether, and the acids. From its acid solution it is precipitated by ammonia. A minute portion of it mixed with lard, and applied to the eye, causes contraction of the pupil, as I have repeatedly seen. One-fiftieth of a grain has endangered the life of an individual. It is the most virulent poison known, not excepting hydrocyanic acid."

The *salts of aconita* have been very imperfectly examined; they



appear to be uncrystallizable, and very soluble in water and in alcohol; they are decomposed by the alkalis, and the aconita is precipitated. This alkaloid has not hitherto been analyzed, nor has its equivalent been accurately ascertained.

DIGITALIA. Leroyer gives the following directions for the extraction of digitalia. (*Bibliothèque Universelle*, xxvi. 102.) He takes "one livre of *Digitalis purpurea*, and first treats it with cold ether, and then with the same agent heated in a close stove, in order that the temperature may be more easily raised. The tinctures obtained in this manner, were, after filtration, of a greenish-yellow color and a bitter taste; the residue from their evaporation has a resinous appearance, and is insupportably bitter, producing upon the tongue a sensation of numbness like that which is experienced from chewing aconite. Exposed to the air, this residuum powerfully absorbs moisture. When taken up by distilled water, it divides into two parts; the vehicle holds one of them in solution, the other is precipitated, and presents all the characters of chlorophylle; the aqueous solution of the ethereal residue reddens turnsol paper. Hydrate of protoxide of lead was then added to neutralize the free acid thus indicated, and to separate from the bitter principle that which is apparently combined with it. The salt of lead thus formed was soluble, and consequently could not be separated from the bitter principle; several earths were tried for the same purpose, but with no better success; it was therefore necessary to resort to another method. After evaporating to dryness the portion treated by the lead, it was again dissolved in highly-rectified ether; by this operation he obtained the bitter principle of digitalis disengaged from those substances with which it was united. By evaporating this solution a brown heavy substance is obtained, that restores, though slowly, the blue of turnsol paper reddened by an acid. If in this last-mentioned character, as well as in its bitterness, it approaches the alkaloids, its extreme deliquescence separates it from them." This deliquescence prevents it from crystallizing in a distinct and permanent manner; but Leroyer thinks that it does crystallize regularly under favourable circumstances. Prevost having placed a drop of the solution of digitalia in alcohol on a piece of glass, and cautiously evaporated it, detected with a microscope numerous and well-defined crystals of various forms. The same observer states, that the basic form of them all appeared to be a straight prism with rhomboidal base.

Another similar process for obtaining digitalia has been given by Planiava, as quoted by Berzelius, (*Lehrbuch*.) but Brault and Poggiale tried it without any satisfactory result. (*Journ. de Pharm.*, xxi. 130.) Another process has been suggested by Lancelot, which consists in treating the aqueous extract of the plant with absolute alcohol, distilling it, dissolving the residue in water, and adding very dilute hydrochloric acid, as long as a yellow precipitate is formed; this, having been dissolved in alcohol, and decolorized by animal charcoal, is left to spontaneous evaporation, when the digitalia forms a granular crystalline deposit. It has an alkaline reaction and an acrid taste. (*Ann. der Pharm.*, xii. 251.) Radig also describes digitalia as a crystallizable alkaloid; (*Pharm. Central Blatt*, 1835, p. 209;) but Trommsdorff, and other chemists, have failed in obtaining it. Radig gives the name of *picrine* to the substance

described by Leroyer. Nothing is as yet known of the ultimate composition, or of the equivalent of the so-called digitalia.

DELPHIA.  $C_{27}H_{19}O_2N$ . This alkaloid was discovered in 1819, by Lassaigue and Feneulle, in the seeds of the *Delphinium staphysagria*, or *Stavesacre*. (*Ann. Ch. et Ph.*, xii. 358.) The simplest mode of obtaining it is that suggested by Berzelius: digest the bruised seeds in water acidulated by sulphuric acid, then add magnesia, collect and dry the precipitate, and digest it in alcohol, by which the delphia is taken up: it may be purified by boiling it, in the state of sulphate, with animal charcoal, and precipitating by ammonia, which throws it down in a gelatinous form: obtained by evaporating its alcoholic solution, it is a crystalline powder, which becomes opaque when dried. (*Lehrbuch*.)

According to Couerbe, (*Ann. Ch. et Ph.*, lii. 359,) pure delphia is obtained by digesting the grey and brown seeds in alcohol, distilling the tincture, digesting the residue in dilute sulphuric acid, filtering, and precipitating by an alkali; the precipitate is dried, dissolved in alcohol, decolored by animal charcoal, and the solution evaporated. The product is then further purified by redissolving it in a large relative proportion of dilute sulphuric acid, and adding nitric acid diluted with its bulk of water, drop by drop; this throws down a brown substance, from which, when it has subsided, the liquor is decanted and precipitated by a very dilute solution of potassa; this precipitate is dissolved in alcohol, the solution is filtered and evaporated, when it leaves a yellow resinous substance, which, having been washed with boiling water to separate a little nitre, is treated by ether; this dissolves the delphia, and leaves it on evaporation; the residue insoluble in ether, has been termed by Couerbe, *Staphisaine*; he regards it as an alkaloid, and assigns to it the formula  $C_{32}H_{23}O_4N$ ; but it is generally regarded as a compound of delphia. According to Couerbe, a pound of the selected seeds yields about 60 grains of the crude delphia; the black seeds are rejected as scarcely containing a trace of the alkaloid.

According to Couerbe pure delphia is not crystallizable; it has a slightly yellow tint, fuses at  $250^{\circ}$ , and is not volatile; it is difficultly soluble in water at any temperature: it is soluble in alcohol, and somewhat less so in ether. It has a peculiarly acrid taste, and excites a burning sensation in the throat. Its salts are very pungent and bitter, and most of them very soluble. The *sulphate* and *acetate* dry into gum-like products; the *nitrate*, and the *hydrochlorate*, form deliquescent saline masses; the *oxalate* is white and lamellar.

Delphia is composed of

|                |    |      |     | Couerbe.   |
|----------------|----|------|-----|------------|
| Carbon .....   | 27 | .... | 162 | .... 77.00 |
| Hydrogen ..... | 19 | .... | 19  | .... 8.89  |
| Oxygen .....   | 2  | .... | 16  | .... 7.50  |
| Nitrogen ..... | 1  | .... | 14  | .... 6.61  |
| <hr/>          |    |      |     |            |
| Delphia .....  | 1  |      | 211 | 100.00     |

CORYDALIA.  $C_{34}H_{22}O_{10}N$ . This alkaloid was discovered by Wackenroder in the *Corydalis tuberosa* and *fabacea*. (*Phil. Mag. and Ann.*, iv. 153.) It is contained in the plant, in combination with malic acid, from which it may be separated by magnesia, and purified by solu-



tion in alcohol. According to Winckler, corydalia is best obtained from the expressed juice of the fresh root, precipitated by acetate of lead; the excess of lead is removed by sulphuric acid, and the alkaloid precipitated by ammonia, dried, dissolved in alcohol, decolored by animal charcoal, and the filtered solution then gently evaporated; on adding a large proportion of water the corydalia is thrown down in a pulverulent form.

Corydalia forms prismatic crystals, soluble in alcohol and ether, but very sparingly so in water; it is tasteless, but its salts are bitter; they are decomposed by the alkalis, and by infusion of galls. The *hydrochlorate* is not crystallizable, but it forms an insoluble double salt with corrosive sublimate. The *acetate* is crystalline. The *sulphate* is crystalline, and the *acid sulphate* gum-like.

Corydalia has been analyzed by Döbereiner with the following results:

|                 |    |      |     |      |        | Döbereiner. |
|-----------------|----|------|-----|------|--------|-------------|
| Carbon .....    | 34 | .... | 204 | .... | 63·75  | .... 63·05  |
| Hydrogen .....  | 22 | .... | 22  | .... | 6·88   | .... 6·83   |
| Oxygen .....    | 10 | .... | 80  | .... | 25·00  | .... 25·80  |
| Nitrogen .....  | 1  | .... | 14  | .... | 4·37   | .... 4·32   |
| <hr/>           |    |      |     |      |        |             |
| Corydalia ..... | 1  |      | 320 |      | 100·00 | 100·00      |

CHELERYTHRIA. This alkaloid was discovered by Probst and Pölex, in the root and unripe seed of the *Chelidonium majus*, and in the root of the *Glaucium luteum*. These roots are digested in water acidulated by sulphuric acid; the liquor is filtered, evaporated, and mixed with ammonia; the brown precipitate which falls is washed, pressed between folds of bibulous paper, and digested in alcohol acidulated by sulphuric acid. This alcoholic solution is then mixed with water, the alcohol distilled off, and the residual liquor precipitated by ammonia: this precipitate is washed, dried by pressure, and digested in ether; the ethereal solution is then evaporated to dryness, and the residue digested in dilute hydrochloric acid, which leaves a resinous substance undissolved, and gives a deep red liquor; this, evaporated to dryness and washed with ether, leaves hydrochlorate of chelerythria, mixed with hydrochlorate of *chelidonia*; the former salt is dissolved by washing with a little water; the latter remains undissolved. From the solution of the hydrochlorate, the chelerythria is precipitated by ammonia as a white powder. Obtained from its ethereal solution it remains as a soft resin-like substance; it is insoluble in water; its solution in alcohol, and in ether, is pale yellow. With acids it forms crimson-colored salts, which are mostly crystalline; they are narcotic and poisonous. Tannine produces in their solutions precipitates which are soluble in alcohol. This alkaloid has not been analyzed.

CHELIDONIA. C<sub>40</sub> H<sub>20</sub> O<sub>6</sub> N<sub>3</sub>. By digesting the sparingly soluble hydrochlorate mentioned in the preceding article, with ammonia, dissolving the precipitate in dilute sulphuric acid, and again throwing it down by hydrochloric acid, it is freed from chelerythria. The purified hydrochlorate is then decomposed by ammonia, and the precipitate dissolved in boiling alcohol, which, on cooling, deposits tabular crystals of *chelidonia*: it is insoluble in water, but soluble in alcohol and in ether; it tastes bitter, and reacts alkaline; its salts are colorless, and those with the mineral acids crystalline. The solutions of the alkaloid are precipitated by tannine. According to Will's analysis, *chelidonia* is composed of

|                 |    |      |     |      |        |      |                |
|-----------------|----|------|-----|------|--------|------|----------------|
| Carbon .....    | 40 | .... | 240 | .... | 68·57  | .... | Will.<br>68·90 |
| Hydrogen .....  | 20 | .... | 20  | .... | 5·71   | .... | 5·62           |
| Oxygen .....    | 6  | .... | 48  | .... | 13·72  | .... | 13·51          |
| Nitrogen .....  | 3  | .... | 42  | .... | 12·00  | .... | 11·97          |
| <hr/>           |    |      |     |      |        |      |                |
| Chelidonia..... | 1  |      | 350 |      | 100·00 |      | 100·00         |

SANGUINARIA. The root of the *Sanguinaria canadensis*, or *Blood root*, contains, according to Dana (*Phil. Mag. and Ann.*, v. 151), an alkaloid, which may be separated as follows: the red alcoholic tincture of the powdered root is mixed with a little ammonia, and poured into water; the matter which subsides yields the alkali to hot alcohol; it must be purified by animal charcoal. It is white, acrid, insoluble in water, but soluble in alcohol and ether, and alkaline to tests. Its salts have a red color. According to Schiel the formula of sanguinaria is  $C_{37}H_{32}O_8N$ . (*Phil. Mag.*, Jan. 1843.)

EMETINA.  $C_{37}H_{27}O_{10}N$ . This term implies the active or emetic principle of *Ipecacuanha*, from which it was procured by Pelletier in 1817. (*Ann. Ch. et Ph.*, iv. 172. *Journ. de Pharm.*, iii. 148, and PELLETIER and DUMAS. *Ann. Ch. et Ph.*, xxiv. 180.) Boullay has detected a similar substance in the root of the *Violet* (*Viola odorata*), (*Journ. de Pharm.*, x. 23,) and Torreri in the root of the *Iris florentina*.

Emetina is obtained by digesting powdered ipecacuanha root, first in ether, by which a fatty matter is abstracted (which gives ipecacuanha its nauseous odor, but which is not emetic), and then in alcohol; this tincture is mixed with magnesia, which throws down impure emetina: the deposit is washed with cold water, and redissolved in boiling alcohol, from which solution the emetina is obtained by evaporation or distillation. Berzelius proposes to digest the powdered root in dilute sulphuric acid, precipitate by magnesia, and separate the emetina by alcohol as before; but this process has not, I believe, been adopted. When an aqueous extract of ipecacuanha is digested in alcohol, a solution is obtained, which when filtered and evaporated to dryness, leaves a deliquescent bitter extract, very soluble in water, and in alcohol. From this, pure emetina may be obtained, according to Merck, by dissolving it in 4 parts of water acidulated by hydrochloric acid, and decomposing the solution by corrosive sublimate, as long as it forms a precipitate. This precipitate is to be well washed with cold water, dissolved in alcohol, and this solution decomposed by sulphuret of barium and filtered; the baryta held in solution is then removed by dilute sulphuric acid, and a considerable quantity of water added; the liquor is then heated to expel the whole of the alcohol, and caustic ammonia added to throw down the emetina, which is washed with cold water and dried.

Thus prepared, emetina forms a white, inodorous, and almost insipid powder, alkaline to tests, and very sparingly soluble in cold water. It is much more soluble in alcohol; but ether, the essential oils, and the caustic alkalis, scarcely act upon it: it fuses at about  $120^{\circ}$ . Concentrated nitric acid converts it in the first instance into a bitter yellow resinoid substance, and ultimately into oxalic acid. It neutralizes the acids, and forms salts which are not crystallizable except with excess of



acid: these salts are mostly very soluble, bitter, and acrid. They give a brown precipitate with chloride of gold, and of platinum, and a white precipitate with corrosive sublimate. Infusion of galls produces with them an insoluble grey precipitate; it has therefore been proposed as an antidote to the effects of emetine. Emetina vomits in the dose of one-sixteenth of a grain, and in a dose of 3 or 4 grains is poisonous. A pharmaceutial preparation is used in France, under the name of *emetine*, obtained by treating an aqueous solution of the alcoholic extract of ipecacuanha by a little magnesia, filtering, and evaporating to dryness. Brandes has described a substance under the name of *Chiococcine*, obtained from the *Chiococca racemosa*, which, according to Von Santon, (as quoted by Liebig), is identical with emetina.

The above formula representing emetina, is deduced from the analysis of Dumas and Pelletier, which is as follows:

|                |    |     |     |     |        | Pelletier. |
|----------------|----|-----|-----|-----|--------|------------|
| Carbon .....   | 37 | ... | 222 | ... | 64.72  | 64.57      |
| Hydrogen ..... | 27 | ... | 27  | ... | 7.87   | 7.77       |
| Oxygen .....   | 10 | ... | 80  | ... | 23.32  | 22.96      |
| Nitrogen ..... | 1  | ... | 14  | ... | 4.09   | 4.30       |
| <hr/>          |    |     |     |     |        |            |
| Emetina.....   | 1  |     | 343 |     | 100.00 | 99.60      |

#### VIII. PIPERINE. ASPARAGINE. CAFFEINE. THEINE.

**PIPERINE.**  $C_{34}H_{19}O_6N$ . This substance was discovered by Oersted, in 1819 (*Journ. de Phys.*, xc.), and afterwards examined by Pelletier; it is obtained from *black pepper*. (*Ann. Ch. et Ph.*, xvi.) Vogel gives the following process for its extraction: Digest 16 ounces of coarsely-powdered pepper for forty-eight hours in twice its weight of water, five times in succession; press out and dry the insoluble portion, and digest it for three days in 24 ounces of alcohol; press out this solution, filter, and evaporate it to the consistence of syrup: crystals are deposited, which are to be freed from adhering resin by ether, redissolved in alcohol, purified by animal charcoal, and recrystallized.

According to Pontet, piperine is best obtained from white pepper, by digesting it in alcohol, sp. gr. 0.833, evaporating, and treating the residuary extract by a solution of potassa, which dissolves resin, and leaves impure piperine, which, after having been washed with water, may be dissolved in absolute alcohol, and crystallized.

Piperine is generally of a pale straw color, and crystallizes in the form of four-sided prisms, insoluble in cold, and slightly soluble in hot water; readily soluble in alcohol, and less so in ether. When quite pure, it is inodorous and tasteless. It fuses at a little above  $212^{\circ}$ , and is not volatile, but when more highly heated yields ammoniacal products. It is regarded as a feeble alkaloid. It absorbs hydrochloric gas to the amount of 13.7 per cent., and the compound fuses, and crystallizes on cooling, but water decomposes it: this hydrochlorate forms definite double salts with the chlorides of platinum and mercury: the platinum compound forms bundles of yellow crystals, soluble in alcohol. Strong hydrochloric and acetic acid dissolve piperine, but on evaporation the acid escapes and leaves the base unchanged. When piperine is treated with bichromate of potassa and sulphuric acid, it disengages carbonic acid, and

a liquid distils over, which reduces nitrate of silver when warmed: the residue smells of bitter almonds, and leaves a greenish uncrystallizable substance when evaporated. (GERHARDT.) Piperine is insoluble in alkaline liquors. The elements of piperine deduced from Regnault's analysis (*Ann. Ch. et Ph.*, LXVIII., 159,) are,

|                |    |     |     |     |        | Regnault. |
|----------------|----|-----|-----|-----|--------|-----------|
| Carbon .....   | 34 | ... | 204 | ... | 71.58  | 71.94     |
| Hydrogen ..... | 19 | ... | 19  | ... | 6.66   | 6.56      |
| Oxygen .....   | 6  | ... | 48  | ... | 16.84  | 16.60     |
| Nitrogen ..... | 1  | ... | 14  | ... | 4.92   | 4.90      |
| Piperine.....  | 1  |     | 285 |     | 100.00 | 100.00    |

ASPARAGINE.  $C_8H_8O_6N_2 + 2HO$ . *Asparamide*. *Altheine*. This principle was discovered in asparagus, by Vauquelin and Robiquet (*Ann. de Ch.*, LVII.); and was shown by Plisson to be identical with a substance found by Robiquet in liquorice root, which he named *Agedoite* (*Ann. de Ch.*, LXXII.), and also with the *Altheine*, discovered by Bacon. (*Ann. de Ch. et Ph.*, XXXIV.) It has been found by Link in the *Ornithogalum*; by Blondeau in the *Symphytum officinale*; and by Piria in the juice of the *climbing vetch*.

It is best obtained from asparagus, the juice of which is expressed, evaporated to the consistency of syrup, and set aside; it deposits crystals, which are purified by solution in water and recrystallization.

Asparagine forms transparent prismatic crystals, which are hard, brittle, of a cooling and somewhat nauseous taste, neither alkaline nor acid; soluble in 58 parts of cold water, and more soluble in hot; insoluble in anhydrous alcohol, and in ether. The crystals lose about 12 per cent. of water when heated: they evolve ammonia when triturated with caustic potassa, but not when merely acted on by a dilute solution of potassa; nitric acid converts them into a bitter matter. According to Liebig, *anhydrous* asparagine consists of

|                      |   |     |     |     |        | Liebig. | Pelouze and<br>Boutron-Charlard. |
|----------------------|---|-----|-----|-----|--------|---------|----------------------------------|
| Carbon .....         | 8 | ... | 48  | ... | 36.36  | 36.74   | 38.70                            |
| Hydrogen .....       | 8 | ... | 8   | ... | 6.06   | 5.94    | 6.54                             |
| Oxygen .....         | 6 | ... | 48  | ... | 36.36  | 36.05   | 32.65                            |
| Nitrogen .....       | 2 | ... | 28  | ... | 21.22  | 21.27   | 22.11                            |
| Anhydrous asparagine | 1 |     | 132 |     | 100.00 | 100.00  | 100.00                           |

The *crystals* include 2 atoms of water; their elements, therefore, are

|                             |    |     |     |     |        | Liebig. | Marchand. |
|-----------------------------|----|-----|-----|-----|--------|---------|-----------|
| Carbon .....                | 8  | ... | 48  | ... | 32.00  | 32.351  | 32.17     |
| Hydrogen .....              | 10 | ... | 10  | ... | 6.66   | 6.844   | 6.66      |
| Oxygen .....                | 8  | ... | 64  | ... | 42.67  | 42.071  | 42.06     |
| Nitrogen .....              | 2  | ... | 28  | ... | 18.67  | 18.734  | 19.11     |
| Crystallized asparagine.... | 1  |     | 150 |     | 100.00 | 100.000 | 100.00    |

According to Pelouze and Boutron-Charlard, (*Ann. Ch. et Ph.*, XXVIII., 188,) when an aqueous solution of asparagine is subjected to a pressure of 3 atmospheres, it becomes aspartate of ammonia.

*Aspartic Acid*.  $C_8H_5O_6N + HO$ . When asparagine is long boiled with hydrated oxide of lead, magnesia, or other bases, it is resolved into ammonia, and into an acid, called *aspartic acid*; and yet asparagine is



not, as might be supposed, an *aspartate of ammonia*, because the alkalis do not immediately separate ammonia from it, nor do acids throw down aspartic acid when added to its aqueous solution.

Aspartic acid was discovered by Plisson, (*Ann Ch. et Ph.*, xxv. 175,) who obtained it by boiling asparagine in baryta water till the evolution of ammonia ceased ; it was then filtered whilst hot, and the baryta immediately precipitated by sulphuric acid ; on cooling, the crystallized aspartic acid was deposited in nacreous crystals. When *aspartate of lead* is decomposed by sulphuretted hydrogen, the aspartic acid is separated, and may be obtained by the action of boiling water upon the precipitate.

Aspartic acid is tasteless and inodorous ; it requires about 125 parts of cold water for solution, but is much more soluble in boiling water. It is insoluble in absolute alcohol, and only very sparingly soluble in common spirit of wine. It is not decomposed by hot nitric acid ; cold sulphuric acid dissolves it, and decomposes it when heated. The *anhydrous acid* consists of

|                              |   |      |     |      |         |
|------------------------------|---|------|-----|------|---------|
|                              |   |      |     |      | Liebig. |
| Carbon.....                  | 8 | .... | 48  | .... | 41·7    |
| Hydrogen .....               | 5 | .... | 5   | .... | 4·4     |
| Oxygen .....                 | 6 | .... | 48  | .... | 41·7    |
| Nitrogen .....               | 1 | .... | 14  | .... | 12·2    |
| <hr/>                        |   |      |     |      | <hr/>   |
| Anhydrous aspartic acid..... | 1 |      | 115 |      | 100·0   |
|                              |   |      |     |      | <hr/>   |
|                              |   |      |     |      | 100·00  |

Liebig therefore regards anhydrous asparagine as an anhydrous *aspartate of ammonia*, which, by the appropriation of an atom of water, passes into *aspartate of oxide of ammonium*.

|                          |  |                |
|--------------------------|--|----------------|
| 1 atom of ammonia .....  | H <sub>3</sub>                               | N              |
| + 1 „ aspartic acid..... | C <sub>8</sub> H <sub>5</sub> O <sub>6</sub> | N              |
| <hr/>                    |  |                |
| = 1 „ asparagine .....   | C <sub>8</sub> H <sub>8</sub> O <sub>6</sub> | N <sub>2</sub> |

According to Liebig, aspartic acid is *bibasic*, the formula of the crystalline or *hydrated acid*, being C<sub>8</sub>H<sub>5</sub>O<sub>6</sub> N, + 2HO ; its ultimate elements therefore are

|                            |                         |       |                                    |                 |
|----------------------------|-------------------------|-------|------------------------------------|-----------------|
| Carbon .....               | 8...48...36·09...36·056 | } = { | Anhydrous<br>aspartic<br>acid..... | 1...115...86·48 |
| Hydrogen .....             | 7... 7... 5·26... 5·311 |       |                                    |                 |
| Oxygen .....               | 8...64...48·12...48·213 |       |                                    |                 |
| Nitrogen.....              | 1...14...10·53...10·420 |       |                                    |                 |
| <hr/>                      |                         |       |                                    |                 |
| Crystallized aspartic acid | 1                       | 133   | 100·00                             | 100·000         |
|                            |                         |       |                                    | <hr/>           |
|                            |                         |       |                                    | 1 133 100·00    |

The salts of the aspartic acid (*aspartates*) are almost all soluble in water. The *aspartates of soda* and of *ammonia* are crystallizable: *aspartate of potassa* is very deliquescent, and uncrystallizable. *Aspartate of lime* and of *magnesia* are gum-like compounds. *Aspartate of baryta* forms small opaque crystals; *aspartate of zinc*, small crystalline grains; *aspartate of copper*, blue needles. A solution of aspartate of potassa produces a precipitate in a solution of basic acetate of *lead*, in nitrate of black oxide of *mercury*, and in nitrate of *silver*.

According to Piria, asparagine is convertible into succinic acid : he also suggests that asparagine and aspartic acid may be represented as *amides of malic acid*. (*Comptes Rendus*, September, 1845.)

CAFFEINE. THEINE.  $C_8H_5O_2N_9$ . *Guaranine*. This important compound is found in *coffee* (the seed of *Coffea Arabica*) and in *tea*, the leaves of *Thea Chinensis*; it is also said to occur in the leaves of *Guarana officinalis* or *Paullinia Sorbilis*, and in *Ilex Paraguayensis*. (*Paraguay tea*.) It is remarkable that one and the same principle, and that belonging to the class of azotised basic bodies, should be found in two such dissimilar vegetables as tea and coffee, infusions of which are used as a beverage over the greater part of the known world, and yet that the peculiar characteristic properties of tea and coffee should not be referable to its presence; at least the action of theine or caffeine on the system is by no means obvious; it is neither narcotic nor in any way poisonous. Liebig has thrown out some suggestions respecting its connection with the secretion of bile, which will be afterwards noticed. But tea and coffee have nevertheless a peculiar influence over the nervous system, which, especially as regards tea, has been ascribed to the presence of an essential oil; something similar may also exist in roasted coffee. Dr. Pereira compares the influence of tea to that of foxglove: "they both occasion watchfulness and act as sedatives on the heart and blood-vessels, and in some constitutions strong tea gives rise to tremor, anxiety, and sleeplessness, possessing a marked influence over the functions of the brain. Like tea, coffee diminishes disposition to sleep, and may be used to counteract the stupor induced by opium, alcoholic liquors, and other narcotics. With some it acts as a laxative, but with others induces constipation." (*On Food and Diet*, pp. 395, 400.)

*Coffee* has been the subject of many chemical researches, and in 1821 a peculiar crystallizable principle was extracted from it by Pelletier and Caventou, and by Robiquet and Runge; previous to which, Schrader had published an analysis of *coffee beans*, of which the following is an abstract. (BERZELIUS, *Lehrbuch*, iv.) He found that 8 ounces of *raw coffee* distilled with water, gave a turbid and odorous distilled water, but the quantity of oil, which probably produced these effects, was too small to collect. The decoction in the retort was filtered, and was then of a yellow-green color: it was evaporated to syrup consistence, and mixed with alcohol, sp. gr. 0.85, as long as this occasioned a precipitate. The filtered solution was then evaporated, and it left 17.58 *per cent.* of a brown transparent extract, (Gmelin's *coffee-bitter*,) soluble in water, and having the characteristic bitter taste of the raw coffee bean. This extract is insoluble in ether and in absolute alcohol, and sparingly soluble in alcohol of 0.84, but its aqueous solution is not precipitated by alcohol. It is not altered by dilute acids or alkalis; but the last deepen its color, and lime-water precipitates it of a green color: the salts of iron produce with it a grass-green color, and a dark-green precipitate falls, soluble in excess of acid. When an alkali is added to its solution, previously mixed with a salt of copper, a fine green precipitate falls, which, carefully prepared without excess of oxide of copper, may be used as a pigment. Acetate of lead precipitates it yellow-green, and protochloride of tin, grey; and when these precipitates are decomposed by sulphuretted hydrogen, the extractive is evolved unchanged. It is neither precipitated by gelatine nor by infusion of galls. It yields ammonia on destructive distillation, and a *crystallized sublimate*.

The substance precipitated by the addition of alcohol to the original decoction of the coffee, was a mixture of 3.6 *per cent.* of brown gum,



and 37 pulverulent extractive. The coffee beans also contain resin, and a fat oil, which may be extracted by alcohol. The insoluble residue constituted two-thirds of the weight of the beans. When burned, coffee beans leave 4 *per cent.* of ash, consisting of carbonate of potassa, (the base of which was combined with a vegetable acid,) sulphate of potassa, chloride of potassium, carbonate and phosphate of lime, magnesia, and the oxides of iron and manganese.

The *crystallized sublimate* alluded to by Schrader has since become the subject of separate examination; it is the *caffeine* of Pelletier and others, and was first obtained by Runge in 1820. There are various methods of obtaining it, and it may be procured in considerable quantity from those who roast large quantities of coffee; it sublimes in a very impure form, but is easily deprived of its adhering impurities. The process generally recommended for its preparation is that of Runge, but others which are preferable will be presently mentioned; it consists in making a strong aqueous infusion of ground raw coffee, adding to it a solution of sugar of lead, which occasions a green precipitate, and leaves the supernatant liquor colorless; the excess of the salt of lead in this liquor is then precipitated by sulphuretted hydrogen, it is filtered, and evaporated; the caffeine remains, and must be treated by animal charcoal to whiten it, and recrystallized.

According to Payen, the following are the components of coffee berries. (*Journ. de Pharm.*, Oct. 1846. *Ch. Gaz.*, Jan. 1847.)

|   |         |
|---|---------|
| Cellulose ( <i>woody fibre</i> ) .....              | 34·000  |
| Water .....   | 12·000  |
| Fat ( <i>oily matter</i> ) .....                    | 13·000  |
| Glucose and dextrine ( <i>sugar and gum</i> ) ..... | 15·500  |
| Legumine and caseine .....                          | 10·000  |
| Chlorogenate of potassa, and caffeine .....         | 5·000   |
| Azotized substance .....                            | 3·000   |
| Free caffeine.....                                  | 0·800   |
| Essential oil .....                                 | 0·003   |
| Mineral substances .....                            | 6·697   |
|   | <hr/>   |
|   | 100·000 |

According to Pfaff, (*Pharm. Central Blatt.*, 1831, p. 423,) the peculiar odor of roasted coffee depends upon the presence of *caffeic acid* in the berry; when this substance is heated it exhales the distinctive aromatic odor of coffee. Caffeic acid is represented by Berzelius as identical with the *chlorogenic acid* of Payen, and as bearing the same relation to the tannine (*caffeotannic acid*) of unroasted coffee, as gallic acid bears to the tannine of the gall-nut. (*Lehrbuch*, iv. 488.)

Caffeine (or theine) forms white silky crystals, soluble in boiling water and alcohol, and deposited in crystalline filaments as these solutions cool; it has no alkaline reaction, yet it appears capable of combining definitely with some of the acids, especially with hydrochloric acid. According to Herzog, a crystallizable sulphate may also be obtained; but others have not succeeded in getting these salts. When caffeine is heated with sulphuric acid it is decomposed. When boiled in baryta water it produces cyanate and formiate of baryta, and ammonia is disengaged. (MULDER.)

The action of nitric acid on caffeine (theine) has been described by Stenhouse. (*Mem. Chem. Soc.*, i. 219 and 239.) When heated together,

a deep yellow liquid is obtained, which, when evaporated to dryness and slightly warmed, gives with ammonia a purple color similar to that of murexide. This is an excellent test for theine. When the yellow liquid is carefully evaporated nearly to the consistence of syrup, it furnishes colorless acicular crystals, which when purified by repeated crystallization have a sweetish taste, and are only very slightly acid. Both this and the red matter appear however to be the products of the imperfect oxidation of theine, for if theine is boiled for some hours with great excess of nitric acid till a drop of the liquor evaporated to dryness is no longer yellow, but white, ammonia produces with it no change of color; and if the greater part of the nitric acid be then distilled off, and the liquor concentrated as before, it affords large shining crystals on cooling, and the mother-liquor appears to consist chiefly of very deliquescent ammoniacal salts. The crystals are gritty and sweetish; they dissolve in about 3 parts of cold, and in much less of boiling water, and are also readily soluble in alcohol and in ether. When purified, they scarcely redden litmus, and the smallest portion of alkali added to their solution renders it alkaline. When heated they sublime, and are deposited in fine shining crystals upon any cold object. They burn with a bright flame. They occasion no precipitate in solutions of nitrate of silver, acetate of lead, or sulphate of iron. When boiled in solution of potassa they give off ammonia. Dr. Stenhouse calls this substance *nitrotheine*; he has not been able to determine its atomic weight, but found it to contain in 100 parts, carbon, 41·87; hydrogen, 4·24; oxygen, 34·50; nitrogen, 19·39.

The components of caffeine, (and of theine,) according to Pfaff and Liebig (*Ann. Ch. et Ph.*, xlix. 303,) are

|                  |   |      |    |      |       |
|------------------|---|------|----|------|-------|
| Carbon.....      | 8 | .... | 48 | .... | 49·5  |
| Hydrogen .....   | 5 | .... | 5  | .... | 5·1   |
| Oxygen .....     | 2 | .... | 16 | .... | 16·5  |
| Nitrogen .....   | 2 | .... | 28 | .... | 28·9  |
| <hr/>            |   |      |    |      |       |
| Caffeine } ..... | 1 |      | 97 |      | 100·0 |
| Theine } .....   |   |      |    |      |       |

Stenhouse formed a double salt by adding chloride of platinum to a hot solution of theine in hydrochloric acid; on cooling, orange-colored crystals are formed, the analysis of which induces him to double the ordinary atomic weight of theine; he represents them by the following formula;  $C_{16}H_{10}O_4N_4, HCl, + PtCl_2$ ; their composition being

|                         |       |      |       |      |        |
|-------------------------|-------|------|-------|------|--------|
| Stenhouse.              |       |      |       |      |        |
| Carbon .....            | 16    | .... | 96    | .... | 23·88  |
| Hydrogen.....           | 10    | .... | 10    | .... | 2·49   |
| Oxygen.....             | 4     | .... | 32    | .... | 7·96   |
| Nitrogen .....          | 4     | .... | 56    | .... | 13·93  |
| Hydrochloric acid ..... | 1     | .... | 37    | .... | 9·21   |
| Chlorine .....          | 2     | .... | 72    | .... | 17·91  |
| Platinum .....          | 1     | .... | 99    | .... | 24·62  |
|                         |       |      |       | .... | 24·48  |
|                         | <hr/> |      | <hr/> |      | <hr/>  |
|                         | 1     |      | 402   |      | 100·00 |

A double chloride of mercury and caffeine is formed when an aqueous or alcoholic solution of caffeine is added to a solution of corrosive subli-



mate; the latter being in excess the fluid remains at first perfectly clear, but in a few seconds solidifies into a mass of small crystals: the formula of this compound, which, with some other combinations of caffeine, has been analysed by Nicholson, is  $C_{16}H_{10}O_4N_4 + 2HgCl$ . (*Mem. Chem. Soc.*, iii. 321.)

*Roasted Coffee*.—According to Cadet (*Ann. de Ch.*, lviii.), coffee roasted to a pale brown color loses 12·3 *per cent.*; to a chestnut brown, 18·5 *per cent.*, and to a black, 23·7 *per cent.* So that the loss of weight in coffee-roasting may be estimated at about 12 to 20 *per cent.* Schrader found, in roasted coffee,

|  |      |
|--|------|
| Extractive matter soluble in water and alcohol, closely resembling that of raw coffee, but browner and deliquescent..... | 12·5 |
| Brown gum .....  | 10·4 |
| Extractive, soluble in water, but insoluble in alcohol .....   | 5·7  |
| Oil and resin .....  | 2·0  |
| Insoluble burned woody fibre.....  | 69·0 |

When roasted coffee was distilled with water, the aroma passed over; the distilled water reddened litmus, and had the agreeable odor of the coffee. When raw coffee is so roasted as to collect the volatile products, a portion of fragrant empyreumatic oil passes over, which, in the ordinary mode of roasting, is lost. According to Chenevix, (*Tilloch's Magazine*, xii. 350,) a portion of tannine is formed during roasting; and Cadet states, that the greatest proportion of tannine is contained in slowly and slightly-roasted coffee, and that, when it is very brown or black, its proportion is much diminished. This product, however, probably depends much upon temperature, for Payssé, Schrader, and Runge, assert that gelatine is not precipitated by an infusion of roasted coffee. Schrader endeavoured to ascertain the particular principle to which the flavor and aroma of roasted coffee are due, by exposing each of the proximate principles of unroasted coffee separately to heat; but he found that no one of them yielded any peculiar flavor, and that the ligneous residue, when roasted, acquired as much of the characteristic flavor as when the other principles were retained; so that the flavor of the roasted coffee must be ascribed to the joint effect of heat upon all the constituents; the caffeine seems to play a very passive part as far as flavor is concerned, and a considerable proportion of it remains unchanged after roasting, whilst another part of it is merely volatilized. It is said that roasted coffee after having been recently ground, is liable to heat, and even ignite, and some mysterious accidents from fire have been referred to this cause.

The flavor of coffee as a beverage depends, in the first place, upon the *roasting*, and, in the next, upon the mode of *making* the infusion; the coffee should be rapidly but well roasted, and it is said to be improved by roasting it in a close vessel; it should be aired, and ground into fine powder immediately before use; it is sometimes *boiled*, and sometimes *infused*; in the former case, the coffee is darker colored, more bitter, and has more of an acid flavor than when infused, and the infusion in a close vessel is more aromatic than that in an open one, especially when the coffee-pot is so managed as to *steam* the powder. The pleasantest flavor is obtained by placing a *sufficient quantity* of finely-ground and freshly-roasted coffee upon a filter, (very coarse filtering paper in a funnel

answers very well,) and pouring boiling water upon it so as to filter quickly into the vessel beneath. When coffee is made by boiling, it is apt to be thick, unless fined by the addition of a little white of egg, or isinglass, which probably carries down the tannine. In *Parker's Coffee Fountain*, a stream of boiling water is forced through a cylindrical vessel containing the ground coffee, by the pressure of steam; it affords excellent coffee, when properly managed. (On the adulterations of roasted and ground coffee, see *Pharm. Journ.*, iv. 85 and 119.)

THEINE. Oudry seems to have been the first who endeavoured to obtain a peculiar principle from tea-leaves, which he says may be separated as follows (BERZELIUS, *Lehrbuch*, iv.): 12 parts of tea were infused for twenty-four hours in 200 of cold water, in which 3 of common salt were dissolved. The infusion was evaporated to dryness, and the residue digested in alcohol of 0·81; the residue of this alcoholic tincture was then dissolved in water, and digested with magnesia, and filtered. On evaporating the filtered liquor to a certain degree of concentration, crystals of *theine* were obtained, and the magnesian residue, digested in alcohol, yielded a further portion.

Stenhouse prepares theine as follows: A decoction of tea is first treated with a slight excess of acetate of lead, which throws down the tannine and almost all the coloring matters it contains; it is then filtered whilst hot, and the clear liquor evaporated to dryness. It forms a dark yellowish mass, which is to be intimately mixed with a quantity of sand, and introduced into Mohr's subliming apparatus and moderately heated for 10 or 12 hours. The theine sublimes in beautifully white anhydrous crystals, deposited upon the paper diaphragm which runs across the apparatus. The only thing to be observed is that the temperature should never rise too high, as the more slowly the operation is conducted, the finer are the crystals and the greater their quantity. When theine is obtained from coffee, the berries should not be roasted, but only slightly dried and then ground or pounded, and repeatedly boiled with water till exhausted. The filtered decoction should first be precipitated while hot by basic acetate of lead; it should then be filtered, and boiled with a little hydrated oxide of lead, which occasions a further precipitate, also to be separated by filtration. The clear liquor is then to be evaporated to dryness, and sublimed in the same way as the extract of tea. From a pound of coffee, Stenhouse obtained an average produce of 15 grains of theine, sometimes not so white as that made from tea, but rendered so by a second sublimation. From hyson tea (green), Stenhouse obtained 1·05 *per cent.* of theine; from Congou (black) 1·02 *per cent.*; from Assam (black) 1·27, and from Tonkay (green) 0·98. But Peligot, guided by the large proportion of nitrogen evolved in the ultimate analysis of tea, was led to suspect a larger proportion of theine, and obtained the following quantities, namely, from hyson, 2·56 to 3·40 *per cent.*, and from gunpowder tea, 2·20 to 4·10 *per cent.*

Peligot also found in the insoluble residue of the tea-leaf, another azotized principle, which he supposes to be *caseine* in combination with tannine. To obtain theine he recommends the following process: Add to the hot infusion of tea, a slight excess of subacetate of lead and then ammonia; boil for some time, and wash the precipitate with boiling



water upon a filter. Pass sulphuretted hydrogen through the filtered liquor to separate the residuary lead, filter, and concentrate by evaporation at a gentle heat, and abundant crystals of theine will be obtained; the mother-liquor yields on evaporation a further produce. By a second solution and crystallization the theine may be obtained pure. By this process 3·84 *per cent.* of theine was obtained from gunpowder-tea, or nearly three times as much as Dr. Stenhouse procured by the process of sublimation. By the incineration of tea Peligot obtained from 5 to 6 *per cent.* of ash, containing oxide of iron.

There seems little doubt that the different teas of commerce are derived from the same plant, and that the age of the leaves and the mode of drying and treating them, are the chief causes of their varied appearance and flavor; the climate, soil, and mode of cultivation may also be concerned in these differences as regards green tea. Warington has shown that the color of *green tea* is artificial, being derived from Prussian blue and a yellow vegetable coloring matter, mixed in some instances with white clay, and in others with sulphate of lime. (*Mem. Chem. Soc.*, ii. 73.)

Some years ago I examined the varieties of tea in common use (*Quart. Journ.*, xii. 201), and found that the quantity of astringent matter precipitable by gelatine is somewhat greater in *green* than in *black tea*, though the excess is by no means so great as the comparative flavors of the two would lead one to expect. The entire quantity of soluble matter is also greater in *green* than in *black tea*, but the extractive matter not precipitable by gelatine is greater in the latter.

The following table shows the respective quantities of soluble matter in water and in alcohol, the weight of the precipitate by isinglass, and the proportion of inert woody fibre in green and black tea of the various market-prices of that time. It will be remarked, that when tea-leaves have been exhausted by water repeatedly affused, alcohol is still capable of extracting a considerable quantity of soluble matter: the alcoholic extract, infused in boiling water, furnishes a liquid which smells and tastes strongly of tea, and which, were it not for the expense of the solvent, and the trouble attending its separation, might perhaps be profitably employed. It is probable that the different degrees of bitterness of different samples of tea, arise from variations in the quantity of theine which they respectively contain.

| One hundred parts of Tea. |              | Soluble in Water. |       | Soluble in Alcohol. |       | Precipitate with Jelly. |        | Inert Residue. |
|---------------------------|--------------|-------------------|-------|---------------------|-------|-------------------------|--------|----------------|
| Green Hyson ....          | 14s. per lb. | 41                | ..... | 44                  | ..... | 31                      | .....  | 56             |
| „                         | 12s. „       | 34                | ..... | 43                  | ..... | 29                      | .....  | 57             |
| „                         | 10s. „       | 36                | ..... | 43                  | ..... | 26                      | .....  | 57             |
| „                         | 8s. „        | 36                | ..... | 42                  | ..... | 25                      | .....  | 58             |
| „                         | 7s. „        | 31                | ..... | 41                  | ..... | 24                      | .....  | 57             |
| Black Souchong            | 12s. „       | 35                | ..... | 36                  | ..... | 28                      | ... .. | 64             |
| „                         | 10s. „       | 34                | ..... | 37                  | ..... | 28                      | .....  | 63             |
| „                         | 8s. „        | 37                | ..... | 35                  | ..... | 28                      | .....  | 63             |
| „                         | 7s. „        | 36                | ..... | 35                  | ..... | 24                      | .....  | 64             |
| „                         | 6s. „        | 35                | ..... | 31                  | ..... | 23                      | .....  | 65             |

The following is the latest analysis of tea, but the proportion of theine is probably underrated. (MULDER, *Pharm. Central Blatt.* for 1838, p. 403.)

|   | CHINESE. |         | JAVANESE. |         |
|---|----------|---------|-----------|---------|
|   | Hyson.   | Congou. | Hyson.    | Congou. |
| Volatile oil .....                                      | 0·79     | 0·60    | 0·98      | 0·65    |
| Chlorophylle .....                                      | 2·22     | 1·84    | 3·24      | 1·28    |
| Wax .....   | 0·28     | 0·00    | 0·32      | 0·00    |
| Resin .....   | 2·22     | 3·64    | 1·64      | 2·44    |
| Gum .....   | 8·56     | 7·28    | 12·20     | 11·08   |
| Tannine .....   | 17·80    | 12·88   | 17·56     | 14·80   |
| Theine .....  | 0·43     | 0·46    | 0·60      | 0·65    |
| Extractive (by water and<br>by hydrochloric acid) ....} | 46·40    | 40·48   | 42·04     | 38·52   |
| Albumine .....  | 3·00     | 2·80    | 3·64      | 1·28    |
| Lignine .....   | 17·08    | 28·32   | 18·20     | 27·00   |
| <hr/>   |          |         |           |         |
|   | 98·78    | 98·30   | 100·42    | 97·70   |
| Salts included in the above                             | 5·56     | 5·24    | 4·76      | 5·36    |

## § XI. ORGANIC COLORING-MATTERS.

UNDER this head a variety of substances are included, of very different characters and composition. Many of them are extremely important in the arts, being used as pigments by painters in water-colors and oil, and extensively employed by dyers and calico-printers. Others are of so fugitive a nature as not to admit of such application, and are chiefly known as giving variety and beauty to the flower, or as communicating to vegetables in general those infinitely varied shades of green which characterize that division of the organic creation. By far the greater number, therefore, of these substances are of vegetable origin, those which are derived from animals being comparatively few, and much more limited in their applications.

Such of these coloring-matters as are soluble in water, often partake of the nature of *extractive matter*, and although fugitive in themselves, are capable of being combined with and fixed, or rendered permanent, by certain *bases* or oxides, which in reference to this particular case, have often been termed *mordants*, (see pp. 1108 and 1202.)

When a solution of *brown* extractive matter, for instance, is mixed with a solution of certain salts of iron, lead, or aluminum, and an alkali is added to the mixture, the metallic oxide falls in chemical combination with the extractive matter, so that the supernatant liquor remains colorless. The same thing happens with other colorific extracts; an infusion of *madder*, for example, when mixed with a solution of alum, and decomposed by an alkali, furnishes a *red* precipitate, and if the alumina be in excess, the residuary solution is perfectly colorless. Other colored solutions present the same phenomena, and the colored precipitates are, in such cases, often termed *lakes*, especially when of a red, pink, or purple tint. In these cases, an attraction is shown to exist between the *metallic oxide* and the *coloring matter*, and it is often the means of conferring a degree of permanence and insolubility on the latter, and modifying its hue. It has already been stated that the various forms of *lignine*, or vegetable fibre, possess a similar attraction for certain oxides: accordingly, if a piece of linen or calico be steeped in a proper solution of such oxide, a combination of the fibre and the oxide will first take place; and then, the fibre thus prepared, if immersed in a solution



of coloring extract, will combine with it, and the color thus become fixed upon the stuff. This, in a few words, is the *theory of the art of dyeing* with the greater number of vegetable colors, which, though in themselves fugitive, and unsusceptible of combination with the linen, cotton, or other material to be dyed, are rendered, to a greater or less extent, fixed and permanent, by the joint attraction of the base or mordant for the fibre and for the color.

*The art of dyeing and calico-printing* has been the subject of several separate works, to which the reader is referred for details. The following are a few of the principal points which bear upon the chemistry of the processes.

In the first place, the goods require to be thoroughly cleansed from all foreign matters and colors, which is effected by washing and *bleaching*. Warm water is at first liberally applied to remove the filth acquired in weaving; the goods, if linen or cotton, are then *bowked*, or boiled with a very weak solution of caustic potassa, washed in large quantities of water, and spread out upon the grass so as to be exposed freely to the joint agencies of light, air, and moisture; this part of the operation, which is tedious, is much curtailed, and frequently entirely superseded, by the careful application of chlorine, or of a weak solution of chloride of lime. The bowking and exposure are alternately repeated as often as necessary; and lastly, the goods are immersed in water slightly acidulated by sulphuric acid, again thoroughly washed, and dried. By these operations the texture of the stuffs is always more or less impaired, especially when chloride of lime is used. In respect to the *theory* of the operation of bleaching, it appears probable, that, in the necessary exposure to water, air, and light, or their substitute *chlorine, nascent oxygen* is developed, and is the destroyer of those portions of coloring matter which are most obstinately retained.

With respect to the nature of the materials or fibre to be dyed, it is found that different substances not only possess very different attractions for dye-stuffs, but they absorb the coloring matter in very different proportions. Wool appears in this respect to have the strongest attraction for coloring substances; silk comes next to it; then cotton; and lastly, hemp and flax.

The simple operation of dyeing is generally performed upon *animal fibre*, such as wool and silk, whilst the more refined operation of printing in patterns and devices of various colors, is chiefly, though by no means exclusively, conducted upon *cotton*, or as it is usually termed, *calico*. It has been above stated, that very few colors are of such a nature as to combine with the fibre without some *intermedium*; but where this is the case, they constitute what have been termed *substantive colors*: but they generally require the intervention of a *base* or *mordant*, and are then called *adjective colors*. The mordants which are most frequently resorted to are, as has already been remarked, salts of alumina, iron, and tin. The substance to be dyed is first impregnated with the mordant, and then passed through a solution of the coloring matter, which is thus fixed in the fibre, and its tint is often modified or exalted by the operation. That a considerable portion of the mordant is retained in the fibre of the calico or cloth dyed, has been proved by the experiments of Dr. Ure. He found that 100 parts of the ashes of Turkey red calico (dyed by an

alum mordant) afforded between 16 and 17 parts of alumina; whereas the ashes of white and washed calico only afforded a trace of that earth. (See two papers, on the incinerated ashes of cotton-wool and calico, dyed by the Turkey red process. *Quart. Journ.*, xxi. 28 and 297.)

*Calico-printing*, which is a more refined and difficult branch of the art, is a species of topical dyeing. In this process *adjective* colors are almost always employed. The mordants, the principal of which are acetate of alumina, and acetate of iron, are first applied to the calico by means of wooden blocks or copper-plates, or cylinders, upon which the requisite patterns are engraved. The stuff is then passed through the coloring bath, and afterwards exposed on the bleaching-ground, or washed. The color flies from those parts which have not received the mordant, and is permanently retained on those parts only, to which the mordant has been applied: variety of colors is produced by employing various mordants, and different coloring materials, and by using them in various states of dilution and combination; in short, there is no instance in which such refined chemical principles and delicate manipulations are brought to bear upon a process of the arts, as in the case of calico-printing.

White spots upon a dark ground are sometimes produced by covering the parts with wax, pipe-clay, or other materials, which prevent the contact of the color; or citric acid, thickened with gum, is applied like a mordant with the block or plate, and prevents the retention of the color. Sometimes the color is discharged in places, by the application of chlorine, a process well illustrated in what are called *Bandana* handkerchiefs, of which an account will be found in the fifteenth volume of the *Quart. Journ.* There is also an interesting series of papers on the subject of calico-printing, in the *Records of Science*, edited by Dr. Thomson, from which some idea may be formed of the refined and complex chemical operations which have been successfully applied to the perfection of that beautiful art.

Besides vegetable and animal colors, others are frequently resorted to, and various *mixtures* are used, by which an infinite variety of *compound colors* are obtained. *Metallic colors* are also constantly employed both in dyeing and calico-printing, and they are not only infinitely various, but often admirably adapted to the processes of the art. Thus, the attraction of oxide of iron for different fibres, which renders it of such importance as a mordant, enables the dyer and printer to avail themselves of *Prussian blue*: and with other metallic mordants, such as oxides of lead, copper, &c., the ferrocyanide of potassium, iodide of potassium, chromate of potassa, arsenio-sulphurets, and various other salts, become the sources of a great variety of beautiful colors.

Instead of first applying the mordant, and afterwards the coloring material, they are occasionally both printed together, but in these cases, particular management is requisite in the selection of the substances employed, and in the mode of their application: when this method is resorted to, the color is often *fixed* by the application of steam.

The coloring matters described in this section are such as have been especial subjects of chemical inquiry and investigation, or are largely and importantly applicable to the arts above mentioned; others either have been or will be elsewhere specifically noticed, and several of them



will be adverted to in the alphabetical enumeration of vegetable products designated "Chemical Botany."

# I. INDIGO.

This invaluable coloring-matter, for which, as a dye-stuff, no adequate substitute has yet been discovered, seems to have been employed in Hindostan at a very early period, but to the Greeks and Romans, it was probably only known as a pigment. It is mentioned by Dioscorides and by Pliny, as an Indian product, under the name of *Indicum*; but it appears not to have been used in Europe, as a dye-stuff, before the middle of the sixteenth century. The Dutch first imported it from India, and made known its valuable qualities. Even as late as the seventeenth century, its use was restricted in different countries. It was prohibited in England during the reign of Elizabeth, and the prohibition continued till the reign of Charles the Second; it was also prohibited in Saxony. "In the Edict," says Dr. Thomson, "it is spoken of as a *corrosive substance*, and called *food for the devil*. Colbert restricted the French dyers to a certain quantity of it." (*Vegetable Chemistry*, 368.)

Within the last twenty years indigo has been an especial object of interest and inquiry among chemists, and as the succeeding outline of the chemistry of indigo will show, it has been minutely and elaborately studied. The full details of these investigations would occupy more space than can here be assigned to them, but the reader will find ample references to the original sources of information. The principal combinations and derivatives of indigo which will be noticed, are the following:—

|                                |   |
|--------------------------------|---|
| Indigo-blue .....              | C <sub>16</sub> H <sub>5</sub> O <sub>2</sub> N                                       |
| Indigo-white .....             | C <sub>16</sub> H <sub>6</sub> O <sub>2</sub> N                                       |
| Hyposulphoindigotic acid ..... | C <sub>16</sub> H <sub>4</sub> O <sub>2</sub> N, S <sub>2</sub> O <sub>5</sub> + HO   |
| Sulphopurpuric acid .....      | C <sub>32</sub> H <sub>10</sub> O <sub>4</sub> N <sub>2</sub> , 2SO <sub>3</sub> + HO |
| Isatine .....                  | C <sub>16</sub> H <sub>5</sub> O <sub>4</sub> N                                       |
| Isatinic acid .....            | C <sub>16</sub> H <sub>6</sub> O <sub>5</sub> N + HO                                  |
| Isatyde .....                  | C <sub>16</sub> H <sub>6</sub> O <sub>4</sub> N                                       |
| Chlorisatine.....              | C <sub>16</sub> H <sub>4</sub> O <sub>4</sub> N Cl                                    |
| Chlorisatinic acid .....       | C <sub>16</sub> H <sub>5</sub> O <sub>5</sub> N Cl                                    |
| Indigotic acid .....           | C <sub>14</sub> H <sub>4</sub> O <sub>5</sub> NO <sub>4</sub> + HO                    |
| Nitropicric acid .....         | C <sub>12</sub> H <sub>2</sub> O, 3NO <sub>4</sub> + HO                               |
| Chrysanic acid .....           | C <sub>28</sub> H <sub>10</sub> O <sub>5</sub> N <sub>2</sub> + HO                    |
| Anthranilic acid .....         | C <sub>14</sub> H <sub>6</sub> O <sub>3</sub> N + HO                                  |
| Aniline .....                  | C <sub>12</sub> H <sub>7</sub> N  |

Indigo, as it occurs in commerce, is usually in the form of cubical pieces, or cakes, friable, and more or less brittle, and of various shades of a peculiar deep blue. When rubbed with a hard body it acquires a coppery appearance, but always furnishes a deep-blue powder: it is tasteless, nearly inodorous, and almost insoluble in water, alcohol, and ether. The masses of indigo have a conchoidal fracture, and the finest samples are those which are lightest and most copper-colored. The great mart for indigo is Bengal, and the other provinces subject to the Presidency of that name, from the 20th to the 30th degree of north latitude; it is also cultivated in the province of Tinnevely, under the Madras Government; in Java; in Luconia, the chief of the Philippine islands;

and in Guatemala and the Caraccas, in Central America. The plants chiefly resorted to as sources of indigo, are different species of *Indigofera*; it is also obtained from other genera, as *Nerium*, *Isatis*, *Marsdenia*, *Polygonum*, *Asclepias*, *Amorpha*, &c.; and Calvert found indigo in the stems of some *Orchideæ*. The state in which indigo exists in the juice of these plants is not well understood; it is in the form of a colorless soluble compound, and is generally obtained by fermenting the bruised plant, during which ammonia is evolved, and a yellow liquor obtained, which, on the addition of lime-water, and exposure to air, deposits the blue indigo in the form of a flocculent precipitate. In America it is said that the dried leaves are infused in hot water, by which a green infusion is obtained, which, on exposure to air, deposits the insoluble blue indigo. (On the details of the manufacture of Indigo, see *Quart. Journ. of Science*, &c., N. S., v. 296, vi. 265; also URE's *Dictionary of Arts*.)

The commercial value of indigo depends upon the proportion of *pure indigo* (*indigo-blue*) which the different samples contain; its average amount is about 50 *per cent*. A rough analysis of the crude indigo may be performed by subjecting it to the successive action of water, alcohol, and hydrochloric acid. (CHEVREUL, *Ann. de Ch.*, LXvi. 20.) 100 parts of Guatemala indigo, thus treated, afforded

|                      |  |  |
|----------------------|--|--|
| To Water .....       | <div> <div>Green matter combined with ammonia .....</div> <div>Deoxidized indigo .....</div> <div>Extract.....</div> <div>Gum .....</div> </div> | 12                                     |
| To Alcohol .....     | <div> <div>Green matter .....</div> <div>Resin .....</div> <div>A trace of indigo .....</div> </div>   | 30                                     |
| To Hydrochloric Acid | <div> <div>Red resin .....</div> <div>Carbonate of lime .....</div> <div>Oxide of iron .....</div> <div>Alumina .....</div> </div>               | <div>6</div> <div>2</div> <div>2</div> |
| Residue .....        | <div> <div>Silica .....</div> <div>Pure indigo .....</div> </div>  | <div>3</div> <div>45</div>             |

Several other methods of determining the value of indigo as a dye-stuff have been suggested by Schlumberger. (*Chem. Gaz.*, March, 1843.)

Indigo was submitted, in 1827, to an interesting series of experiments by Berzelius (*Ann. Ch. et Ph.*, xxxvi. 310), who found its usual constituents to be four distinct substances: viz., 1. *gluten*; 2. a *brown substance*, apparently resembling extract; 3. a *red substance*, which gives a gray sublimate when heated in close vessels; 4. *indigo-blue*. 1. The substance which Berzelius terms *gluten*, is soluble both in alcohol and water, and was obtained by digesting powdered indigo in dilute sulphuric acid, neutralizing the solution by chalk, filtering, evaporating to dryness, and digesting the residue in alcohol. 2. The *brown matter* was taken up from the indigo (freed as above from gluten) by potassa, and precipitated by sulphuric acid. 3. Upon the indigo, thus purified by dilute acid, and by the action of solution of potassa, strong alcohol was digested, which took up a *red substance*, insoluble in water and alkalis, but soluble in concentrated sulphuric acid, and in nitric acid, and which, when heated *in vacuo*, yielded a gray crystalline sublimate. 4. The substance remaining after the action of the above solvents is, excepting a little silica, the



real coloring-matter of the indigo, or *indigo-blue*, and is that which forms a purple vapor and sublimate when indigo is heated.

*Indigo-blue. Indigotine.*  $C_{16}H_5O_2N$ . In order to obtain perfectly pure *indigo-blue*, Berzelius treats the indigo of commerce successively with hydrochloric acid, weak solution of potassa, and hot alcohol, to remove the foreign substances above mentioned; the remaining indigo-blue is then thoroughly mixed with twice its weight of freshly-slaked lime, and the mixture put into a bottle capable of holding 150 times the quantity of indigo operated on; the bottle is then filled up with boiling-hot water, and 4 parts of crystallized protosulphate of iron added for every 3 of indigo; it is then securely stopped so as to be air-tight, and having been well shaken, is set aside for several hours. In this way the indigo-blue, which is insoluble, is converted into *indigo-white*, which is soluble in the lime-water, producing a yellow liquor. This yellow liquor is then poured off, mixed with dilute hydrochloric acid, and left for a long time exposed to air; the acid retains the lime, and other substances in solution, while the indigo-blue is deposited, and may be freed from hydrochloric acid and chloride of calcium, by washing with water.

Fritzsche's process for obtaining pure indigo-blue, is as follows: 4 ounces of finely-pulverized crude indigo, and the same quantity of grape-sugar, or of honey, is mixed with a little alcohol (sp. gr. 0.860) and put into a bottle of the capacity of 10 pounds; to this is added 6 ounces of a concentrated solution of caustic soda, and the bottle filled up with hot alcohol, well stopped, and shaken, and then set aside. After some hours the clear red liquor is drawn off from the insoluble deposit, by means of a syphon, into another bottle, the mouth of which is loosely covered so as to allow the admission of air; after some days, the indigo-blue is precipitated, and after having been washed with alcohol, is to beedulcorated with hot water. (LÖWIG, *Chem. d. Organ. Verbind.*, i. 960. *Chem. Gaz.*, February, 1843.)

Indigo-blue may also be obtained by *sublimation*: for this purpose Crum uses two shallow platinum capsules, (the covers of crucibles) about three inches diameter, and of such form that when placed with their concave sides inwards, they were about three-eighths of an inch distant in the middle. About the centre of the lower lid, were placed 10 grains of coarsely bruised indigo, the cover was then put on, and the flame of a spirit-lamp applied beneath the indigo, which soon began to disengage vapor, accompanied by a hissing noise; when this ceased, the heat was withdrawn, and the apparatus allowed to cool; the sublimed indigo was found crystallized, chiefly upon the inner surface of the cover: in this way he obtained from 18 to 20 *per cent.* of the indigo employed. (*Ann. of Phil.*, 2 Ser., v. 82.)

A better mode of obtaining sublimed indigo has been suggested by T. Taylor. (*Chem. Gaz.*, January, 1843.) It consists in mixing powdered indigo with about half its weight of plaster of Paris, and water enough to make a thin paste, which is to be spread in the form of a strip about two inches broad and an eighth of an inch thick, upon a metal plate, and gently dried; the heat of a large spirit-lamp is then applied beneath the plate, when the indigo smokes and gives off its dense purple vapor, which condenses in brilliant prisms or plates, forming a velvety coating over the heated part: the lamp is thus to be applied successively, till the

whole has been adequately heated, and when cold, the sublimate may be swept off without disturbing the subjacent mass.

Berzelius observes in regard to *sublimed indigo*, that it always requires boiling in alcohol, in order to free it from a portion of empyreumatic oil.

The *precipitated indigo-blue*, as obtained by the first processes, has a peculiar deep blue, and at the same time copper color, and frequently appears slightly crystalline. The *sublimed indigo-blue* forms flat needles and four-sided prisms, which, viewed at a particular angle, have a peculiar and intense copper color; but when lying in heaps, are of a rich brown. Sometimes the crystals are in broad thin plates, which, when viewed by transmitted light, are of a splendid blue. The vapor of indigo-blue is transparent, and of a fine reddish-violet tint, somewhat resembling the vapor of iodine. The sublimation takes place at about  $550^{\circ}$ , and the melting-point of the substance, its point of volatilization, and that at which it is decomposed, are very near each other. The sp. gr. of sublimed indigo-blue is 1.35. When the crystals are heated in an open vessel they sublime without residue, in reddish-violet vapor; in close vessels, as the heat advances, the vapor acquires a scarlet tinge, and then becomes orange-colored; a small quantity of a peculiar *basic empyreumatic oil* (*aniline*) is also formed, and charcoal is deposited. (CRUM.)

Heated upon platinum-foil, indigo-blue gives a purple smoke, and if the heat be rapidly augmented it fuses, boils, and burns with a bright flame, giving off much smoke, and leaving a carbonaceous residue, which may be entirely consumed. Indigo-blue is insipid and inodorous, and neither basic nor acid. It is perfectly insoluble in water and in ether, and boiling alcohol merely dissolves a trace of it. Hot olive-oil, and oil of turpentine, acquire from it a blue tint, but on cooling they deposit the minute portion which they had apparently dissolved. Dilute acids and alkaline solutions have no action upon it.

Indigo-blue has been analyzed by Crum, (*Ann. of Phil.*, 2nd Ser., v. 82,) by Dumas, (*Ann. Ch. et Ph.*, lxiii. 267,) by Erdmann, (*Erdmann and Marchand's Journ.*), and by Laurent (*Revue Scientif.*, Sept., 1844.) The formula generally assigned to it, deduced from these analyses, is  $C_{16}H_5O_2N$ ; the following are the details:—

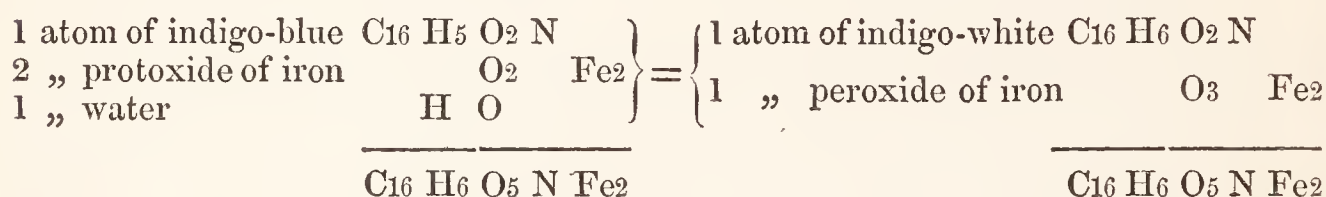
|                   | Crum. |      |     |      | Dumas. |      |        |      | Erdmann. |      |        |       | Laurent. |  |  |  |
|-------------------|-------|------|-----|------|--------|------|--------|------|----------|------|--------|-------|----------|--|--|--|
| Carbon .....      | 16    | .... | 96  | .... | 73.28  | .... | 73.22  | .... | 73.28    | .... | 73.99  | ....  | 73.30    |  |  |  |
| Hydrogen.....     | 5     | .... | 5   | .... | 3.82   | .... | 2.92   | .... | 3.82     | .... | 3.80   | ....  | 3.88     |  |  |  |
| Oxygen .....      | 2     | .... | 16  | .... | 12.21  | .... | 12.60  | .... | 12.21    | .... | 11.56  | }.... | 22.82    |  |  |  |
| Nitrogen .....    | 1     | .... | 14  | .... | 10.69  | .... | 11.26  | .... | 10.69    | .... | 10.65  |       |          |  |  |  |
| Indigo-blue ..... | 1     |      | 131 |      | 100.00 |      | 100.00 |      | 100.00   |      | 100.00 |       | 100.00   |  |  |  |

*Indigo-white. Indigogene. Deoxidized Indigo. Reduced Indigo.*  $C_{16}H_6O_2N$ . It has been above stated, that by the action of certain deoxidizing agents, such as protoxide of iron, and grape-sugar, indigo-blue is rendered soluble in an alkaline liquor. If the yellow solution, obtained by the action of lime and protosulphate of iron upon indigo and water, be decomposed by an acid under the cautious *exclusion of oxygen*, a white precipitate is formed: this is *indigo-white*; and it is best obtained by syphoning the yellow liquor into a stopper bottle previously filled with hydrogen or carbonic acid gas, and containing some acetic or



dilute hydrochloric acid, the syphon itself being previously filled with water deprived of air. Under these circumstances a white, flocculent, and often somewhat crystalline precipitate, falls; it should be most carefully excluded from all contact of air, and allowed to subside; the supernatant liquor must then be decanted, the precipitate collected upon a filter in an atmosphere of hydrogen or of carbonic acid, edulcorated with water freed from air, pressed in folds of bibulous paper, and dried *in vacuo*. (BERZELIUS. See also directions for the preparation of indigo-white, by Dumas, *Ann. Ch. et Ph.*, 3ème Sér., ii. 209.)

Liebig decomposes the yellow liquor, in a bottle containing a mixture of hydrochloric acid and sulphite of ammonia, washes the precipitate with a dilute solution of sulphurous acid or of sulphite of ammonia, and dries it at  $212^{\circ}$ , in a stream of hydrogen. The conversion, in these cases, of indigo-blue into indigo-white, by means of a protosalt of iron, is not a simple reduction, but is probably attended by the decomposition of water, the oxygen of which is transferred to the protoxide of iron, and the hydrogen to the indigo-blue; thus we have



Indigo-white, when dried, always, has a greenish or bluish tint, though it probably would be perfectly white if quite pure. It has a silky fracture, is destitute of taste and odor, and shows no acid reaction. It is not volatile, and when heated *in vacuo* it gives off a little water, indigo-blue sublimes, and carbon remains, no permanent gas being evolved. It is insoluble in pure water, and in dilute acids. It forms a yellow solution in alcohol and in ether, and these solutions, when exposed to air, gradually deposit indigo-blue. When moist it speedily passes into indigo-blue under the influence of air; and even when dry, it slowly acquires a blue color: this change goes on even *in vacuo*, in consequence probably of the air retained in the pores of the substance being sufficient to communicate to it a blue tinge. When it is gradually heated in the air, the whole mass suddenly acquires a dark-purple color, *burning*, as Berzelius expresses it, into indigo-blue.

Indigo-white acts in the manner of an acid, in respect to bases. It forms yellow solutions with the alkalis and alkaline earths, which, when exposed to air, become immediately covered with an iridescent copper-colored film of indigo-blue, whilst the liquor underneath acquires at first a peculiar reddish-green tint, and then gradually passes into blue. When a solution of alumina is precipitated by an alkaline solution of indigo-white, the precipitate becomes presently blue, and if collected upon a filter and dried, it forms a dark-blue powder which glitters in the sunshine, as if it were crystalline; when heated, indigo-blue easily sublimes, and the remaining alumina retains a greenish tint. These compounds with metallic oxides are best obtained by adding a crystallized salt of the basis to a saturated alkaline solution of the indigo-white, in a phial entirely filled, and well stopped. In this way, the salts of protoxide of iron, protoxide of tin, and oxide of lead, give white precipitates, which

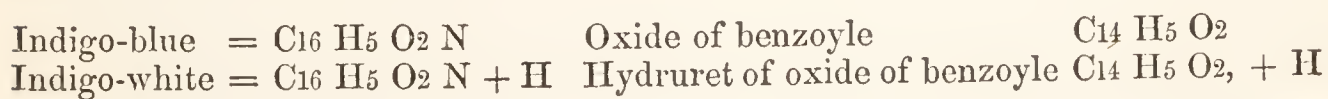
are instantaneously blued by the air. The iron compound gives no indigo-blue by sublimation. The lead compound, which is somewhat crystalline, deflagrates slightly when heated, and leaves reduced lead; the tin compound gives a sublimate of indigo-blue. The precipitate by neutral persulphate of iron is dark-brown, and permanent if there be excess of indigo-white in the liquor; but if the salt of iron is in excess, its oxide is reduced to the state of protoxide, and the precipitate becomes blue. The precipitates with the protosalts of manganese, and of cobalt, are green, and give no sublimate of indigo-blue when heated. The salts of copper immediately produce a blue color, and their oxide is reduced to suboxide. With nitrate of silver the precipitate is first brown, then black, and is not affected by air: when heated, indigo-blue sublimes and metallic silver remains. This precipitate is probably a mixture of indigo-blue and metal. (LÖWIG.)

Indigo-white was originally regarded as deoxidized indigo, or as a lower oxide of the base of indigo-blue; the processes, therefore, by which indigo-white is obtained, were considered as cases of deoxidization, and it was supposed that simple oxidization was the cause of the change of the white into the blue oxide.

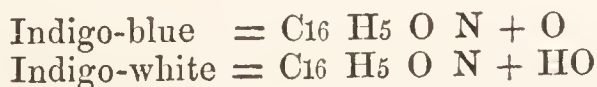
But Dumas' analysis (*Ann. Ch. et Ph.*, Lxiii. 269), the correctness of which has not been questioned, has shown that in passing into white indigo, blue indigo acquires an additional atom of hydrogen, the proportion of oxygen remaining the same in both; the accepted composition of white indigo being as follows:—

|                    |    |     |        |        |        |
|--------------------|----|-----|--------|--------|--------|
|                    |    |     |        |        | Dumas. |
| Carbon.....        | 16 | 96  | 72.72  | 72.79  |        |
| Hydrogen .....     | 6  | 6   | 4.55   | 4.58   |        |
| Oxygen .....       | 2  | 16  | 12.12  | 22.63  |        |
| Nitrogen .....     | 1  | 14  | 10.61  |        |        |
| <hr/>              |    |     |        |        |        |
| Indigo-white ..... | 1  | 132 | 100.00 | 100.00 |        |

Two hypotheses, therefore, have been suggested in respect to the *rational formulæ* of these products. The one regards indigo-white as a *hydruret* of indigo-blue, and compares the relation of the two substances to that subsisting between oxide and hydruret of oxide of benzoyle: thus we have



The other view regards indigo-blue as an *oxide*, and indigo-white as a *hydrate*, of one and the same base, giving



It is further obvious that as concerns these compounds, a common radical (*Anyle*,  $\text{C}_{16} \text{H}_5 \text{N} = \text{An}$ ) may be assumed as their basis; in this case, indigo-white would be a *hydrated protoxide of anyle*,  $= \text{An O} + \text{HO}$ , and indigo-blue, the *anhydrous deutoxide*,  $= \text{An O}_2$ . These hypotheses have their respective advantages in their applications to certain of the indigo-compounds.



ACTION OF SULPHURIC ACID ON INDIGO-BLUE. *Hyposulphoindigotic Acid. Sulphindigotic Acid. Sulphindylic Acid.* [ $\text{C}_{16}\text{H}_4\text{O}_2\text{N} + \text{S}_2\text{O}_5$ ] + HO. When 1 part of indigo-blue is digested for 3 days with 15 parts of oil of vitriol, in a stopped bottle, and at a temperature between  $120^\circ$  and  $140^\circ$ , a deep blue solution is obtained, without any evolution of sulphurous acid. This solution mixes perfectly with water, and if the preceding proportions have been adhered to, there is no sediment; it is a solution of *hyposulphoindigotic acid*. (*Sulphindylic acid* of Dumas.) When evaporated to dryness, the acid remains in the form of a dark blue substance, which is deliquescent, and has a peculiar odor; it forms a dark blue solution with water and alcohol, of a sour and somewhat astringent taste. If woollen cloth be immersed in the diluted blue liquor, it becomes effectually dyed, and the liquor itself is entirely deprived of color. By digesting the blue wool in a solution of carbonate of ammonia, a solution of *hyposulphindigotate of ammonia* is obtained, with which several other salts of the blue acid may be prepared. Dumas gives the following directions for the preparation of the *hyposulphindigotate of potassa*. (*Chim. app. aux Arts*, viii. 19.) A concentrated solution of acetate of potassa is poured into an aqueous solution of the concentrated blue liquor, which produces a precipitate of sulphate and hyposulphindigotate of potassa; the whole is poured upon a sheet of filtering paper placed upon a linen strainer, and left to drain for 24 hours: the liquor which passes ought to be clear and almost colorless. The precipitate is collected, and diffused through a concentrated solution of acetate of potassa, and the filtration repeated; in this way the sulphate of potassa is abstracted from the blue salt, but as some of the solution of the sulphate still remains mixed with it, the operation with the solution of acetate of potassa requires to be repeated, taking care that the precipitate is perfectly diffused through the liquor before it is again thrown upon the strainer. When the sulphate of potassa is thus entirely removed, the acetate of potassa may be washed out of the blue salt by means of common alcohol; lastly, the salt is to be dried *in vacuo*. The formula usually assigned to this salt is [ $\text{C}_{16}\text{H}_4\text{O}_2\text{N}$ ,  $\text{S}_2\text{O}_5$ , KO], in which the indigo has lost an atom of hydrogen, and the 2 of sulphuric acid have lost 1 atom of oxygen: but Dumas represents it, perhaps less obviously and conveniently, by the formula [ $\text{C}_{16}\text{H}_4\text{O N}$ ,  $\text{SO}_3$ , + KO,  $\text{SO}_3$ ], according to which, the salt is a *double sulphate*, analogous to a *sulphovinate*. This view seems to be founded upon some supposed analogy between indigo-blue and alcohol; thus, adopting the formula  $\text{C}_{16}\text{H}_4\text{N O} + \text{HO}$  for indigo-blue, the body  $\text{C}_{16}\text{H}_4\text{N O}$  would be the counterpart of *oxide of ethyle*. (The analyses of the preceding potassa-salt, and of the corresponding baryta-salt, are given by Dumas, in his 4th Memoir "on Chemical Types." *Ann. Ch. et Ph.*, 3ème Sér., ii. 204.)

*Salts of the Hyposulphoindigotic Acid.* These combinations are best obtained by direct saturation; they are generally red by transmitted light. The solutions of the hyposulphoindigotates of the alkalis are precipitated by the common sulphates, and by most other salts, and are only sparingly soluble in spirit of wine. When the blue acid is saturated with carbonate of potassa, and a little of the carbonate added in excess, the mixture assumes a gelatinous appearance: sulphate, and

other salts of potassa, with the exception of saltpetre, when added to a mixture of hyposulphoindigotic acid and free sulphuric acid, produce the same effect; the resulting precipitate when dried, shrinks, and acquires a copper color. The potassa salt is soluble in boiling water, but the greater part of it again separates as the solution cools: the ammonia and the soda salt, resemble it. Hyposulphoindigotate of lime, and of baryta, are difficultly soluble in cold water; in hot water they form a dark blue solution, which deposits the greater part of the salt on cooling. Wool acts as a basis to this acid, and the resulting compound again yields the acid to other bases.

When zinc or iron is put into the aqueous solution of this acid, it loses its color, without the evolution of hydrogen, but regains it when exposed to air. Sulphuretted hydrogen does not affect it at common temperatures, but when heated to  $120^{\circ}$ , sulphur is thrown down, and the blue color disappears. Protochloride of tin, and all those substances which convert indigo-blue to indigo-white, act similarly upon this acid. When protosulphate of iron is dissolved in a solution of a neutral hyposulphoindigotate, the color is not disturbed, nor is it affected when part of the oxide of iron is thrown down by an alkali, but the moment that the whole of the oxide is precipitated and excess of alkali present, decoloration ensues; on again adding excess of acid, the blue returns.

*Sulphopurpuric Acid.*  $[C_{32}H_{10}O_4N_2 + 2SO_3] + HO$ . When 1 part of indigo is triturated with 7 or 8 parts of oil of vitriol, (or better, with the fuming sulphuric acid,) the mixture, upon the addition of water, deposits sulphopurpuric acid in the form of a purple powder, which must be immediately washed upon a strainer with water acidulated by hydrochloric acid, till all traces of free sulphuric acid are removed, and then very carefully dried; if not heated above  $356^{\circ}$ , it retains water, and if heated above  $392^{\circ}$ , it begins to be decomposed; Dumas recommends drying it in an oil-bath between those temperatures, and *in vacuo*.

This acid is soluble in pure water, and in alcohol. By digestion in oil of vitriol, it passes into the hyposulphoindigotic acid. It only saturates 1 atom of base. It is constituted, when *anhydrous*, of

|                           |    |      |      |      |        | Dumas.    |
|---------------------------|----|------|------|------|--------|-----------|
| Carbon.....               | 32 | .... | 192  | .... | 56.14  | .... 56.5 |
| Hydrogen .....            | 10 | .... | 10   | .... | 2.93   | .... 2.9  |
| Oxygen .....              | 4  | .... | 32   | .... | 9.35   | .... 9.4  |
| Nitrogen .....            | 2  | .... | 28   | .... | 8.19   | .... 8.1  |
| Sulphuric acid.....       | 2  | .... | 80   | .... | 23.39  | .... 23.1 |
| <hr/>                     |    |      |      |      |        |           |
| Sulphopurpuric acid ..... | 1  |      | 342. |      | 100.00 | 100.0     |

*Salts of the Sulphopurpuric Acid.* When an aqueous solution of sulphopurpuric acid is added to any salt, the acid of the salt is set free, and a *sulphopurpurate* is precipitated, which in appearance resembles the acid, but the solubility of which varies with the base. Neither acids nor heat interfere with the precipitation. These salts are more soluble in alcohol than in water, and like pure indigo-blue, are decolorized by reducing agents, and regain color on exposure to air. The compounds with lime, magnesia, oxide of zinc, protoxide of iron, and oxide of copper, only communicate a pale blue color to water.

*Isatine.*  $C_{16}H_5O_4N$ . This compound appears to have been simul-



taneously discovered by Erdmann and by Laurent. (*Ann. Ch. et Phys.* 3ème Sér., iii. 355, 371, 462. *Erdmann and Marchand's Journ.*, xxiv. 11, 30.) It is the result of the oxidizement of indigo, by chromic or by nitric acid. A dilute aqueous solution of chromic acid is gradually added to pulverised indigo; the mixture is heated nearly, but not quite, to its boiling-point, and a brown solution is obtained. The chromic acid should only be of such strength as freely to dissolve the indigo; for if it be too strong, carbonic acid is evolved, oxide of chromium is precipitated, and isatine is not formed. The brown solution should be filtered whilst hot, and the isatine crystallizes as the liquor cools. When nitric acid is used, it is gradually added to the finely-powdered indigo, so as to form a paste, which is then moderately heated and constantly stirred, when a brisk effervescence ensues; the acid is to be added till the blue color disappears; water is then added, and the mixture boiled and quickly filtered whilst hot; in about 12 hours reddish crystals of isatine are deposited, and on evaporating the mother-liquor a further portion may be obtained. This first product is washed with a very weak solution of ammonia, which abstracts a brown resinous matter; it is then washed with distilled water, and finally, dissolved in boiling alcohol and crystallized.

Isatine, thus prepared, forms brilliant, reddish-brown, prismatic crystals, inodorous, sparingly soluble in cold, but more abundantly in hot water, and readily soluble in alcohol, but less so in ether. The alcoholic solution communicates a peculiarly unpleasant and permanent odor to the cuticle. When isatine is heated in a tube, a portion of it sublimes, but the greater part is decomposed, leaving a difficultly combustible coal. Heated in the air it fuses, exhales a suffocating vapor, burns with a brilliant flame, and leaves much difficultly combustible carbon. By the action of chlorine and bromine it forms *chlorisatine*, and *bichlorisatine*, and *bromisatine*, and *bibromisatine*. It dissolves in solution of ammonia and of potassa, and of sulphuretted hydrogen and sulphuret of ammonium, producing peculiar compounds, which have been especially examined by Erdmann and Laurent.

Isatine is composed of

|                |       |      |       |      |        | Laurent.  | Erdmann.    |
|----------------|-------|------|-------|------|--------|-----------|-------------|
| Carbon.....    | 16    | .... | 96    | .... | 65·30  | .... 65·2 | .... 65·3   |
| Hydrogen ..... | 5     | .... | 5     | .... | 3·40   | .... 3·5  | .... 3·4    |
| Oxygen .....   | 4     | .... | 32    | .... | 21·77  | .... 21·8 | } .... 31·3 |
| Nitrogen ..... | 1     | .... | 14    | .... | 9·53   | .... 9·5  |             |
| <hr/>          | <hr/> |      | <hr/> |      | <hr/>  | <hr/>     | <hr/>       |
| Isatine.....   | 1     |      | 147   |      | 100·00 | 100·0     | 100·0       |

Isatine therefore, is indigo + 2 atoms of oxygen; or  $C_{16}H_5O_2N + O_2$ .

*Isatinic Acid.*  $C_{16}H_6O_5N + HO$ . Isatine forms a purple solution with caustic potassa, which becomes yellow when heated, and furnishes, on evaporation, a crystalline salt, in small hard prisms, (*isatinate of potassa*.) When a solution of this salt is decomposed by acetate of lead, a white precipitate falls (*isatinate of lead*), which, diffused through water, and decomposed by sulphuretted hydrogen, yields a colorless acid solution. When this is allowed to evaporate spontaneously *in vacuo*, it deposits a white and scarcely crystalline powder, which is *hydrated isatinic acid*. When this is boiled in water it is resolved into water and

isatine, the liquor at the same time acquiring a brown color, and depositing crystalline isatine on cooling. The greater number of the *isatinates* are insoluble or difficultly soluble in water, and may be obtained by double decomposition, by means of isatinate of potassa. *Anhydrous isatinate of silver* is composed of

|                          |    |     |     |     |        | Erdmann.    | Laurent.    |
|--------------------------|----|-----|-----|-----|--------|-------------|-------------|
| Carbon .....             | 16 | ... | 96  | ... | 35.29  | ...         | 35.22       |
| Hydrogen .....           | 6  | ... | 6   | ... | 2.20   | ...         | 2.48        |
| Oxygen .....             | 5  | ... | 40  | ... | 14.71  | } ... 22.51 | } ... 62.30 |
| Nitrogen .....           | 1  | ... | 14  | ... | 5.15   |             |             |
| Oxide of silver .....    | 1  | ... | 116 | ... | 42.65  |             |             |
| Isatinate of silver .... | 1  |     | 272 |     | 100.00 | 100.00      | 100.00      |

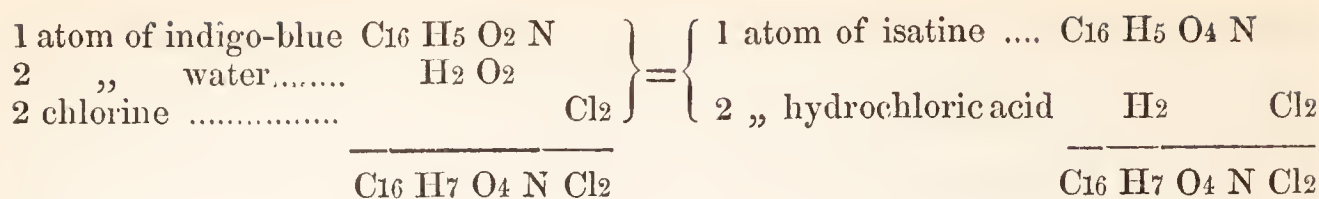
The *crystallized isatinate of silver*, obtained by mixing boiling solutions of nitrate of silver and isatinate of potassa, from which it crystallizes on cooling, is represented by the formula  $C_{16}H_6O_5N, + AgO, + HO$ . (LAURENT.)

*Isatyde*,  $C_{16}H_6O_4N$ , was obtained by Laurent by adding a little sulphuret of ammonium to a hot alcoholic solution of isatine, and leaving the mixture in a stopped phial; small white crystals soon began to form, and in the course of eight days produced a gray deposit, which was washed with alcohol, and was found by the microscope to consist of a mixture of minute prismatic and octohedral crystals; the latter were sulphur, and were separated by means of sulphuret of carbon. The remaining *isatyde* is insoluble in water, and only sparingly soluble in boiling alcohol and ether, which deposit it in microscopic crystals on cooling. It undergoes various transformations when acted on by potassa. (See LAURENT.) Its analysis led to the following formula, which represents it as isatine + 1 atom of hydrogen.

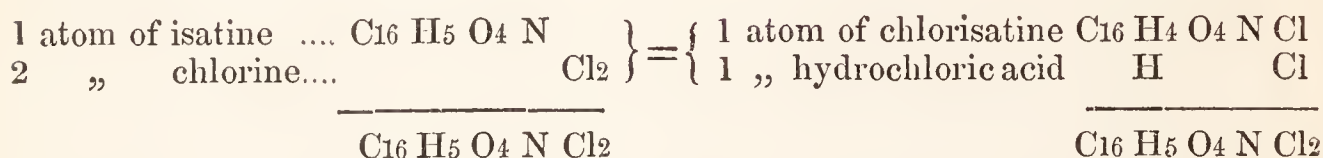
|                |    |       |     |       |        | Laurent. |
|----------------|----|-------|-----|-------|--------|----------|
| Carbon .....   | 16 | ..... | 96  | ..... | 64.86  | 65.11    |
| Hydrogen ..... | 6  | ..... | 6   | ..... | 4.06   | 4.13     |
| Oxygen .....   | 4  | ..... | 32  | ..... | 21.62  | 21.26    |
| Nitrogen ..... | 1  | ..... | 14  | ..... | 9.46   | 9.50     |
| Isatyde.....   | 1  |       | 148 |       | 100.00 | 100.00   |

*Action of Chlorine and of Bromine upon Indigo and upon Isatine.* Indigo is not acted upon by chlorine in its dry state, but when chlorine is passed through indigo diffused in water, the blue color gradually disappears, and a yellow solution is obtained containing several products, which have been examined by Erdmann, and by Laurent. (*Ann. Ch. et Ph.*, 3ème Sér., iii. 355, and 371.) Among them, *chlorisatine*,  $C_{16}H_4O_4NCl$ , and *bichlorisatine*,  $C_{16}H_3O_4NCl_2$ , (substitution compounds,) are the most important. These products are termed by Laurent, consistently with his nomenclatural principles, *chlorisatinase* and *chlorisatinese*; but Erdmann's terms are quite as explanatory, and more consistent with the commonly accepted methods of designation. The first effect of the action of chlorine upon the indigo is probably the formation of isatine, and of hydrochloric acid:



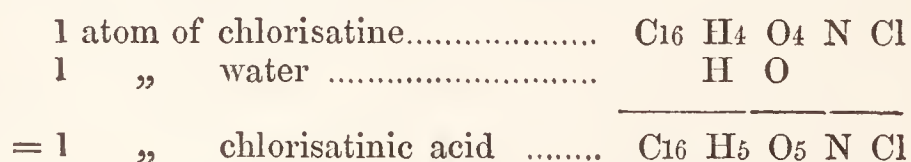


And then,



When the crude product of the action of chlorine on indigo and water is distilled, it yields volatile substances which go over with the water, and crystallize in the neck of the retort and in the receiver, and a solution of chlorisatine and bichlorisatine remains. These two products may be separated by means of boiling alcohol, from which the chlorisatine principally separates on cooling, whilst the bichlorisatine remains dissolved. By repeating the solutions in and crystallizations from alcohol, the chlorisatine and bichlorisatine may be very perfectly separated. When isatine is diffused through boiling water, and chlorine passed through the boiling liquor, exposed at the same time to the direct action of the solar rays, it acquires a yellow color and passes into chlorisatine, no bichlorisatine being, under such circumstances, formed.

Chlorisatine,  $C_{16} H_4 O_4 N Cl$ , crystallizes in yellow prisms, and brilliant scales; it is inodorous, bitter, almost insoluble in cold water, but abundantly soluble in hot water. 100 parts of alcohol, sp. gr. 0·830, dissolve 0·45 of chlorisatine, forming a dark orange-colored solution, which communicates a disagreeable adherent odor to the cuticle. It is neither acid nor alkaline. It may be heated to  $320^\circ$  without decomposition; at higher temperatures it exhales fumes having the odor of those of burning indigo, and burns with flame. It is soluble in a warm solution of caustic potassa, and the liquor yields crystals of *chlorisatinate of potassa*, the chlorisatine, under the influence of the alkali, having combined with the elements of an atom of water, to form *chlorisatinic acid*.



The *chlorisatinates*, and the combinations produced by the action of ammonia on chlorisatine and chlorisatinic acid, have been described in detail by Erdmann and by Laurent.

*Bichlorisatine*,  $C_{16} H_3 O_4 N Cl_2$ , is retained in the alcoholic solution which has deposited the more crystallizable and less soluble chlorisatine; it forms brilliant pink needles when purified from chlorisatine by solution in weak alcohol and crystallization. It yields *bichlorisatinate of potassa* by the action of a warm solution of potassa, the formula of the *bichlorisatinic acid* being, according to Laurent,  $C_{16} H_4 O_5 N Cl_2 = N C_{16} \frac{H_4}{Cl_2} O_5$ .

*Bromisatine*,  $C_{16} H_4 O_4 N Br$ , and *Bibromisatine*,  $C_{16} H_3 O_4 N Br_2$ , are produced by the action of bromine upon indigo, or upon isatine.

According to Hofmann, bromisatine is easily formed by the action of an aqueous solution of bromine upon isatine; whereas bibromisatine is best obtained from isatine and pure bromine. These compounds closely resemble the corresponding chlorine combinations, and by the action of potassa, they produce *bromisatinic* and *bibromisatinic acids*.

I must here refer to the details given by the authorities already quoted, for a further account of an almost infinite variety of other products which are the results of the actions of oxygen, chlorine, and bromine, upon indigo, or which arise out of, or are connected with those actions. Liebig and other systematic writers have tabulated these results, and an abridged statement of them will be found in GREGORY'S *Outlines*, p. 475, which renders the subject as intelligible as its nature admits of. They are described in detail by Löwig, in his *Chemie der Organischen Verbindungen*.

ACTION OF NITRIC ACID UPON INDIGO. *Indigotic Acid. Anilic Acid. Nitrosalicylic Acid. Nitrospiroylic Acid.*  $C_{14}H_4O_9N, +HO$ ; or  $C_{14}H_4O_5, NO_4 + HO$ . This compound has already been mentioned (p. 1386) as appertaining to the *salicylic series*. It was discovered by Fourcroy and Vauquelin, but they regarded it as benzoic acid. Buff (*Schweigger's Journ.*, li. 38, and liv. 163) and Dumas (*Ann. Ch. et Ph.*, liii. 270) afterwards determined its composition; Marchand obtained it by the action of nitric acid upon spiroylic acid (*Erdmann and Marchand's Journ.*, xxvi. 385); and Gerhardt produced it in the same way, from salicine. (*Ibid.*, xxxviii. 84.) It is best obtained by introducing into a sufficiently capacious tubulated retort, 2 parts of nitric acid, sp. gr. 1.28, previously diluted with its weight of water, and gradually adding to it, 1 part of bruised indigo; the retort has a receiver adapted to it, and is heated in a sand-bath; violent action soon ensues, which sometimes requires the removal of the retort from the sand-heat. When this has terminated and the retort cooled, a resinous substance, mixed with crystals of indigotic acid, floats upon the liquor; this is treated with hot water to separate the indigotic acid, the solution of which is returned to the acid liquor in the retort, and the mixture concentrated by distillation, so as to crystallize on cooling. During the process, water, having the odor of hydrocyanic acid and containing a little nitric and nitropicric acid, passes over; the residue, left in a cool place, deposits crystals of indigotic and nitropicric acid, which are to be redissolved in boiling water, and on cooling, the indigotic acid crystallizes in slender needles, but the nitropicric is retained in solution. To free this acid from adhering resinous and other impurities, it must be dissolved in boiling water, and saturated by recently precipitated carbonate of lead; the filtered liquor then deposits *indigotate of lead* on cooling, and affords a further portion on evaporation: the purified indigotate of lead is then dissolved in boiling water, decomposed by dilute sulphuric acid, and the liquor filtered whilst hot, so that on cooling it may deposit the indigotic acid, which forms slender prisms, yellow whilst humid, but white when dry. To obtain the acid perfectly white, a cold saturated solution of indigotate of lead must be decomposed by nitric acid; the crystals, as well as the mother-liquor, are then colorless. The composition, and further properties of this acid are stated above. (p. 1387.)



II. *Nitropicric Acid. Picric Acid. Nitrophenisic Acid. Carbazotic Acid. Indigo-bitter.*  $C_{12}H_2O, 3NO_4, + HO$ . This compound seems first to have been noticed by Hausmann, in 1788. Welter afterwards obtained it as one of the products of the action of nitric acid upon silk, (*Annales de Chimie*, xxix. 301,) and it was known under the name of *Welter's bitter principle*. Hatchett noticed the formation of *artificial tannine* in this process. (*Phil. Trans.*, 1805.) Chevreul first described its character, as an *acid* (*Annales de Chimie*, Lxxii. 117); it was then studied and analyzed by Liebig (*Ann. Ch. et Ph.*, xxxvii. 286), and afterwards more accurately examined by Dumas (*Ann. Ch. et Ph.*, Lxiii. 271. *Ibid.*, 3ème Sér., ii. 228.) Laurent obtained it from one of the products of the distillation of coal tar, and gave its rational formula  $C_{12} \overset{H_2}{3NO_4} O, + HO$ . (See p. 502.)

The following is Liebig's process for the preparation of this acid: A portion of the best indigo is to be broken into small fragments, and gently heated with eight or ten times its weight of nitric acid, of moderate strength. It will dissolve, evolving an abundance of nitrous vapor, and swelling up in the vessel. After the scum has fallen, the liquid is to be boiled, and nitric acid added as long as any disengagement of red vapor is occasioned by it. When the liquid has become cold, a large quantity of semi-transparent yellow crystals will be formed, and if the operation has been well conducted, no artificial tannine or resin will be obtained. The crystals are to be washed with cold water, and then boiled in water sufficient to dissolve them. If any oily drops of tannine form on the surface of the solution, they must be carefully removed by touching them with filtering-paper. Then, filtering the fluid and allowing it to cool, yellow brilliant crystalline plates will be obtained, which will not lose their lustre by washing. To obtain the substance perfectly pure, the crystals must be redissolved in boiling water, and neutralized by carbonate of potassa. Upon cooling, a salt of potassa will crystallize, which should be purified by repeated crystallizations. On mixing the first mother-liquor with water, a considerable brown precipitate will be obtained, which being dissolved in boiling water, and neutralized by carbonate of potassa, will also furnish a quantity of the salt. All the potassa salt obtained in these operations is to be redissolved in boiling water, and nitric or hydrochloric acid added; as the solution cools, the nitropicric acid will be observed to form very brilliant plates of a clear yellow color, generally in equilateral triangular forms. Sometimes crystals are not formed after the action of nitric acid on the indigo, in which case the liquor must be evaporated, and water added, when the acid will precipitate, and must be purified as already described. Four parts of indigo yield one of this acid.

When nitropicric acid is heated, it fuses, and is volatilized without decomposition; when subjected to a sudden strong heat, it inflames without explosion, its vapor burning with a yellow flame, and a carbonaceous residue remaining. It is but little soluble in cold water, but much more in boiling water; the solution has a bright yellow color, reddens litmus, has an extremely bitter taste, and acts like a strong acid on metallic oxides, dissolving them and forming peculiar crystallizable salts. Ether and alcohol dissolve it readily. When fused in chlorine or with iodine,

it is not decomposed, nor does solution of chlorine affect it. Cold sulphuric acid has no action on it; when hot it dissolves it, but water separates it again without alteration. Boiling hydrochloric acid does not affect it, and nitrohydrochloric acid only with great difficulty.

The following are the results of the analyses of this acid in its *crystallized* or *hydrated* state; the equivalent of the *anhydrous acid* being = 220.

|  |    |     |     |     |        |     | Marchand. | Schunck. | Dumas. | Laurent. |        |
|--|----|-----|-----|-----|--------|-----|-----------|----------|--------|----------|--------|
| Carbon .....                           | 12 | ... | 72  | ... | 31.45  | ... | 31.43     | ...      | 31.97  | ...      | 31.86  |
| Hydrogen.....                          | 3  | ... | 3   | ... | 1.31   | ... | 1.36      | ...      | 1.36   | ...      | 1.52   |
| Oxygen .....                           | 14 | ... | 112 | ... | 48.91  | ... | 48.72     | ...      | 48.16  | ...      | 48.00  |
| Nitrogen .....                         | 3  | ... | 42  | ... | 18.33  | ... | 18.49     | ...      | 18.51  | ...      | 18.62  |
| <hr/>                                  |    |     |     |     |        |     |           |          |        |          |        |
| Crystallized ni- }<br>tropicric acid } | 1  |     | 229 |     | 100.00 |     | 100.00    |          | 100.00 |          | 100.00 |

*Nitropicrate of Ammonia.*  $\text{NH}_4 \text{O}, \text{C}_{12} \text{H}_2 \text{O}, 3\text{NO}_4$ . This salt forms prismatic crystals, which are yellow by transmitted, but iridescent by reflected light. It is readily soluble in water. It deflagrates slightly when heated.

*Nitropicrate of Potassa.*  $\text{KO}, \text{C}_{12} \text{H}_2 \text{O}, 3\text{NO}_4$ . This salt crystallizes in long yellow quadrilateral needles, semi-transparent and very brilliant, yellow by transmitted, but blue and having a metallic lustre by reflected light. (SCHUNCK, *Ann. der Pharm.*, xxxix. 1.) It dissolves in 260 parts of water at  $60^\circ$ , but in much less boiling water: a saturated boiling solution becomes, on cooling, a yellow crystalline mass, from which scarcely any fluid will run. Strong acids decompose this salt; yet when an alcoholic solution of the acid is added to a solution of nitre, crystallized nitropicrate of potassa, after some time, precipitates. Alcohol does not dissolve this salt. When it is gradually heated in a glass tube, it first fuses, and then suddenly explodes, breaking the tube to atoms; traces of charcoal are observed on the fragments. This salt precipitates a solution of the protonitrate of mercury, but not salts containing the peroxide, nor those of copper, lead, cobalt, iron, lime, baryta, strontia, or magnesia. The slight solubility of this salt supplies a method of testing and separating potassa in a fluid. The saturated solution of the salt at  $50^\circ$  is not troubled by chloride of platinum. The salt contains no water of crystallization. According to Braconnot it has been used with success in the treatment of intermittents. Its composition is,

|                         |   |      |     |      | Marchand. |      | Laurent. |      | Schunck. |      |        |
|-------------------------|---|------|-----|------|-----------|------|----------|------|----------|------|--------|
| Potassa .....           | 1 | .... | 48  | .... | 17.91     | .... | 17.25    | .... | 17.41    | .... | 17.56  |
| Nitropicric acid.....   | 1 | .... | 220 | .... | 82.09     | .... | 82.75    | .... | 82.59    |      | 82.44  |
| <hr/>                   |   |      |     |      |           |      |          |      |          |      |        |
| Nitropicrate of potassa | 1 |      | 268 |      | 100.00    |      | 100.00   |      | 100.00   |      | 100.00 |

*Nitropicrate of Soda;*  $\text{Na O}, \text{C}_{12} \text{H}_2 \text{O}, 3\text{NO}_4$ ; crystallizes in fine silky yellow needles, having the general properties of the salt of potassa, but soluble in from 20 to 24 parts of water, at  $59^\circ$ .

*Nitropicrate of Lime,*  $\text{Ca O}, \text{C}_{12} \text{H}_2 \text{O}, 3\text{NO}_4 + 5\text{HO}$ , obtained like the salt of baryta, forms flattened quadrangular prisms, very soluble in water, and detonating like the salt of potassa.

*Nitropicrate of Baryta,*  $\text{Ba O}, \text{C}_{12} \text{H}_2 \text{O}, 3\text{NO}_4 + 5\text{HO}$ , is obtained by boiling carbonate of baryta, and the acid, with water. It crystallizes



in quadrangular prisms of a deep color, and dissolves easily in water. When heated, it fuses, and at a temperature of  $212^{\circ}$  loses 4 atoms of water; at a red heat it is decomposed with very powerful explosion, producing a vivid yellow flame: the explosion is as powerful as that of fulminating silver. A solution of chloride of potassium, to which nitropicrate of baryta has been added, produces a precipitate of the potash-salt. When this neutral nitropicrate of baryta is kept for some hours at a temperature of  $640^{\circ}$ , it becomes anhydrous, and along with its water it loses a portion of its acid. The residue, treated with water, leaves a brown and almost basic salt,  $= 2\text{Ba O}, \text{C}_{12} \text{H}_2 \text{O}, 3\text{NO}_4$ , which at a dull red heat is also violently explosive.

*Nitropicrate of Strontia* also forms a neutral, and a basic salt, resembling those of baryta.

*Nitropicrate of Magnesia* crystallizes in needles, with 5 atoms of water, 4 of which it loses when heated, and then explodes violently.

*Nitropicrates of Lead.* Laurent and Marchand have described several of these salts, namely, a neutral nitropicrate,  $= \text{PbO}, \text{C}_{12} \text{H}_2 \text{O}, 3\text{NO}_4$ , and 5 basic salts, composed as follows:

1.  $5\text{PbO} + \overline{\text{Npcr}}$
2.  $3\text{PbO} + \overline{\text{Npcr}} + 3\text{HO}$
3.  $5\text{PbO} + 2\overline{\text{Npcr}} + 8\text{HO}$
4.  $2\text{PbO} + \overline{\text{Npcr}} + \text{HO}$
5.  $3\text{PbO} + 2\overline{\text{Npcr}} + 3\text{HO}$

They are all powerfully explosive by heat, and the second salt explodes by percussion. The neutral *nitropicrate of lead* forms double salts with *nitrate* and with *acetate of lead*. (SCHUNCK. RIECKHER.)

*Nitropicrate of suboxide of Mercury* requires 1200 parts of water for solution.

*Nitropicrate of Silver.*  $\text{Ag O}, \text{C}_{12} \text{H}_2 \text{O}, 3\text{NO}_4 + \text{HO}$ . This salt is best formed by mixing a boiling hot solution of nitropicrate of potassa with nitrate of silver, and evaporating; it forms stellated groups of yellow acicular crystals, and contains, both according to Dumas and to Marchand, an atom of water of crystallization. This salt does not explode, but merely deflagrates when heated.

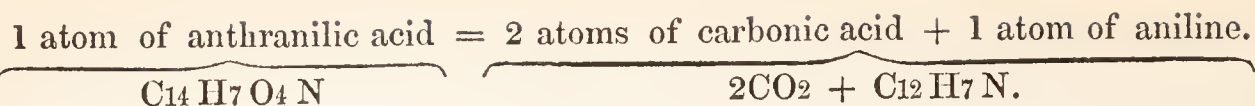
*Nitrorubinic Acid. Nitrohæmic Acid.* (*Hämatinsalpetersäure*; BERZELIUS: from *αἷμα*, blood.) This acid is formed when an intimate mixture of nitropicric acid and protosulphate of iron is digested with water and hydrate of baryta. The protoxide of iron is converted into peroxide at the expense of the nitropicric acid, and the new acid forms with the baryta a salt of a *blood-red* color. After having removed the excess of baryta by carbonic acid, the liquor was precipitated by acetate of lead, the lead-salt decomposed by sulphuretted hydrogen, and the whole heated and filtered whilst hot. On evaporating the filtered liquor, small brown crystals of the acid are deposited; they are nearly tasteless, and detonate slightly when heated, evolving cyanide of ammonium, and leaving a shining coal which burns without residue. It is very sparingly soluble in water, forming a yellow solution; its salts are of a blood-red color when in solution, and burn like gunpowder when heated. The composition of this acid has not been ascertained.

**ACTION OF THE ALKALIS UPON INDIGO.** When pulverized indigo is added to a concentrated boiling solution of caustic potassa, (sp. gr. 1.45) it dissolves rapidly, and the liquor assumes a brown color; on further evaporation brilliant crystals begin to appear, and on cooling, a concrete mass is produced, which with water gives a brown, and with alcohol, a deep green solution. The aqueous solution resembles the "indigo bath" or alkaline solution of indigo-white above described (p. 1478), and soon becomes covered with an iridescent pellicle of indigo-blue, which is partly crystalline. If the greater part of the potassa be neutralized by a mineral acid, so as to form a blue-green precipitate, a golden-yellow liquor is obtained on filtration, which on being supersaturated by acetic acid, deposits a voluminous brown flocculent precipitate, which contains, according to Fritsche, a new substance which he terms *Chrysanilic acid*. To separate this acid, the precipitate is agitated with its bulk of ether, which yields a golden-yellow solution, and which when evaporated, leaves it in the form of a reddish-yellow substance. As obtained by drying it when precipitated from its alkaline solution by an acid, it is of the color of kermes. Its solution in the alkalis is yellow, and becomes green on adding excess of alkali, and covered by a green pellicle, which under the microscope appears somewhat crystalline. Boiled in the dilute mineral acids it yields a red solution, which on cooling deposits bluish-black acicular crystals, and *anthranilic acid* remains dissolved in the liquor. Neither the chrysanilic acid, nor even the crystals just noticed, appear to be of definite composition, but Fritsche has assigned to the acid the formula  $C_{28}H_{10}O_5N_2 + HO$ . (*Ann. der Pharm.*, xxxix. 79.)

*Anthranilic Acid.*  $C_{14}H_6O_3N + HO$ . To prepare this acid, indigo-blue is kept boiling in a solution of caustic potassa, (sp. gr. 1.35,) a little water being occasionally added as the liquor thickens. Before the whole of the indigo has disappeared, finely-pulverized peroxide of manganese is added to the boiling liquor, till a portion of it, diluted with water, no longer deposits indigo-blue; if it be then supersaturated by an acid, it only yields a slight brown precipitate, and holds in solution *anthranilate of potassa*, and a considerable excess of caustic potassa. In this state it is to be diluted with boiling water, supersaturated by dilute sulphuric acid, and filtered. The filtered liquor is then neutralized by potassa, and evaporated to dryness. The residue contains sulphate and anthranilate of potassa, and a brown coloring matter; the two latter are then abstracted by hot alcohol, which leaves the sulphate of potassa. On distilling off the alcohol, dissolving the residue in water, and supersaturating the solution by acetic acid, orange-colored crystals of impure anthranilic acid are deposited; these are then converted into *anthranilate of lime*, which is dissolved in hot water, and acetic acid added to the hot solution: on cooling, the *hydrated anthranilic acid* forms transparent yellow foliated crystals, terminated by dihedral summits. A saturated solution of the salt of lime, decomposed by acetic acid, deposits acicular crystals of anthranilic acid, which are white, and very bitter.

When anthranilic acid is gently heated, it forms a crystalline sublimate resembling benzoic acid. When mixed with powdered glass, and subjected to rapid distillation, it is resolved into carbonic acid and *aniline*.





Anthranilic acid is sparingly soluble in cold water, but very soluble in alcohol and in ether, and these solutions have the taste of benzoic acid, and an acid reaction. (LIEBIG.) It has been analyzed by Liebig and by Fritsche, with the following results:—

|                                   |    |     |     |     |        | Fritsche. | Liebig. |     |       |        |
|-----------------------------------|----|-----|-----|-----|--------|-----------|---------|-----|-------|--------|
| Carbon.....                       | 14 | ... | 84  | ... | 61.31  | ...       | 61.82   | ... | 62.13 |        |
| Hydrogen .....                    | 7  | ... | 7   | ... | 5.11   | ...       | 5.09    | ... | 5.16  |        |
| Oxygen .....                      | 4  | ... | 32  | ... | 23.36  | ...       | 22.25   | }   | ...   | 32.71  |
| Nitrogen.....                     | 1  | ... | 14  | ... | 10.22  | ...       | 10.84   |     |       |        |
| <hr/>                             |    |     |     |     |        |           |         |     |       |        |
| Crystallized anthranilic acid ... | 1  |     | 137 |     | 100.00 |           | 100.00  |     |       | 100.00 |

When impure anthranilic acid, obtained as above described, is boiled with milk of lime, it forms a yellow limpid solution, which, decolorized by animal charcoal, deposits on cooling colorless rhombohedric crystals of *anthranilate of lime*, sparingly soluble in cold, but copiously in boiling water. When a solution of this salt of lime is added to a boiling solution of nitrate of silver, lamellar crystals of *anthranilate of silver* are obtained, which are anhydrous, and in which the atom of water of the hydrated, or crystallized anthranilic acid, is replaced by an atom of oxide of silver, their formula being  $\text{AgO} + \text{C}_{14} \text{H}_6 \text{O}_3 \text{N}$ . (LIEBIG.)

*Aniline. Crystalline. Cyanole.*  $\text{C}_{12} \text{H}_7 \text{N}$ . This compound has already been mentioned (under the name of *Kyanole*) as a product of the distillation of coal tar (p. 503), from which it was obtained by Runge. (*Poggend. Ann.*, xxxi. 65; xxxii. 308.) It had previously been detected by Unverdorben in the empyreumatic oil obtained by the dry distillation of bone, and certain other animal substances. (*Poggend.*, viii. 397.) Fritsche procured it by the distillation of anthranilic acid; and Zinin (*Erdmann and Marchand's Journ.*, xxvii. 109) by the action of sulphuretted hydrogen upon nitrobenzide; he termed it *Benzidam*, representing it as an *amide of benzine*, by the formula  $\text{C}_{12} \text{H}_5, + \text{NH}_2$ . The identity of this product with the preceding was first shown by Hofmann, who pointed out other cases of its formation, and has added much to our knowledge of its properties and compounds. (*Ann. der Pharm.*, xlvii., liii., and lvii., and *Mem. Chem. Soc.*, ii. 249, 266, 306, and iii. 26.)

The preparation of aniline from indigo, or rather, from anthranilic acid, has been already mentioned: but it is best obtained by the dry distillation of an alkaline anthranilate, as by distilling the compound obtained by adding indigo to a hot solution of caustic potassa. The product requires to be purified by distilling it off potassa in a current of carbonic acid gas.

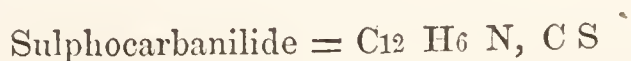
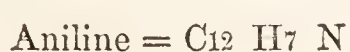
Aniline is a colorless oil-like liquid, possessing a very high refractive power: it has a strong disagreeable odor, and a hot aromatic flavor. It boils, according to Hofmann, at  $360^\circ$ , (according to Fritsche, at  $445^\circ$ ,) but it evaporates rapidly at common temperatures, and the greasy spot which it produces on paper quickly disappears; it remains perfectly fluid at  $0^\circ$ ; its specific gravity at  $60^\circ$  is 1.020. It is soluble to a certain extent in cold water, and the solution becomes turbid when heated: it is

soluble in all proportions, in alcohol, ether, aldehyde, acetone, sulphuret of carbon, and in fat and volatile oils. It has no alkaline reaction on turmeric or on reddened litmus, but it changes the violet color of dahlia paper to green. When a glass rod dipped in hydrochloric acid is held over its aqueous solution, white fumes are produced, resembling those formed by ammonia. Aniline dissolves sulphur when aided by heat, and on cooling, deposits it in prismatic crystals; it also dissolves phosphorus, camphor, and colophony, but not copal or caoutchouc; like kreasote, it coagulates albumen.

Aniline is composed of

|               |    |      |    |      |        | Fritsche.<br>(Aniline.) |       | Zinin.<br>(Benzidine.) |       | Hofmann.<br>(Kyanole.) |         |
|---------------|----|------|----|------|--------|-------------------------|-------|------------------------|-------|------------------------|---------|
| Carbon .....  | 12 | .... | 72 | .... | 77.42  | ....                    | 78.05 | ....                   | 77.23 | ....                   | 77.307  |
| Hydrogen .... | 7  | .... | 7  | .... | 7.53   | ....                    | 7.60  | ....                   | 7.50  | ....                   | 7.720   |
| Nitrogen .... | 1  | .... | 14 | .... | 15.05  | ....                    | 14.98 | ....                   | 14.84 | ....                   | 14.973  |
| <hr/>         |    |      |    |      |        |                         |       |                        |       |                        |         |
| Aniline ..... | 1  |      | 93 |      | 100.00 |                         |       |                        |       |                        | 100.000 |

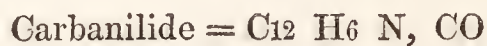
When aniline is exposed to air it absorbs oxygen, and becomes yellow, brown, and resinous. A few drops of fuming nitric acid added to anhydrous aniline produces a fine blue color, which on slightly heating the mixture passes into yellow, and violent action ensues, sometimes followed by explosion; otherwise, the liquor passes through various hues, and crystals of nitropicric acid are ultimately formed in it. When aniline is added to a solution of permanganate of potassa, peroxide of manganese is thrown down, and oxalic acid and ammonia are formed. When aniline is added to a solution of chloride of lime, a beautiful violet-blue color is produced, which is reddened by the addition of an acid; this reaction is very characteristic of aniline. When chlorine is passed into aniline, it assumes the consistence of tar, and on distilling this product, a compound passes over, composed of  $C_{12}H_6NCl$ , and which is identical with Erdmann's *Chlorindatmit*; this is succeeded, when the water has passed over, by a yellow crystalline oil, which is Erdmann's *Chlorindoptenic acid*,  $= C_{12}H_2OCl_3 + HO$ . (*Chlorophenismic acid* of Laurent.) When the vapor of hydrated cyanic acid is passed into aniline, or when a solution of sulphate of aniline is mixed with cyanate of potassa, a crystalline product is obtained, represented by the formula  $C_{14}H_8O_2N_2 = C_{12}H_7N, HO, CyO$ ; that is, according to Hofmann, *urea*, in which the ammonia is substituted by an equivalent of aniline. (*Mem. Chem. Soc.*, iii. 26.) By the action of aniline upon sulphuret of carbon, Hofmann obtained a crystallized compound, which he terms *sulphocarbanilide*; its analysis yielded numbers corresponding with the formula  $C_{13}H_6NS$ ; that is, aniline which has lost an equivalent of hydrogen, and assumed in its place, a compound of carbon and sulphur,  $= CS$ , which corresponds in composition to carbonic oxide.



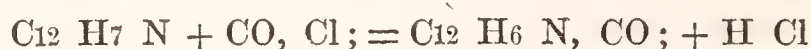
When sulphocarbanilide is boiled for some hours in an alcoholic solution of potassa, sulphuret of potassium is formed, and a new substance is deposited on cooling, which crystallizes in large brilliant needles, and has the formula  $C_{13}H_6NO$ ; it is therefore formed by an exchange of the sulphur of the former compound, with the oxygen of the potassa.



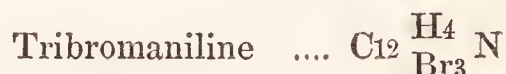
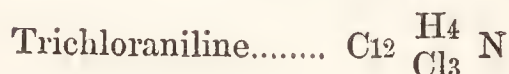
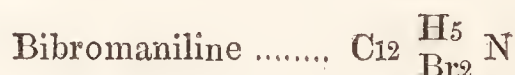
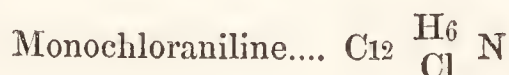
Many other oxides produce the same effect as potassa. This new compound, which is an indifferent body, may be represented as aniline which has lost one equivalent of hydrogen and assumed the elements of carbonic oxide.



Hofmann also obtained carbanilide by the action of aniline upon chlorocarbonic acid; much heat was evolved, and on cooling, crystals of carbanilide, mixed with hydrochlorate of aniline, were formed.



Aniline, when pure, is remarkable for its tendency to form crystallizable combinations; (*Crystalline*). Its salts separate from alcohol, or from their hot aqueous solutions, in the form of white inodorous crystals, which assume a rose-color on exposure to air. It unites directly with the acids, and, as is the case with ammonia, its salts with the oxyacids include an atom of water. The salts of aniline are decomposed by the fixed alkalis, and also by ammonia at common temperature; but when heated, aniline expels ammonia. These salts have been principally studied by Hofmann and by Fritsche, and the *phosphates of aniline* have been analysed and described by Nicholson. (*Mem. Ch. Soc.*, iii. 227.) Aniline combines with chlorine, and with bromine, and the compounds are basic: there are three of each, which may be represented as follows:



These combinations have been analysed and described by Hofmann. Hofmann and Muspratt have also obtained a compound, which they term *nitroaniline*, and which may be represented as  $\text{C}_{12} \frac{\text{H}_6}{\text{NO}_4} \text{N}$ . It forms splendid acicular crystals.

## II. LICHEN BLUES. ARCHIL. LITMUS.

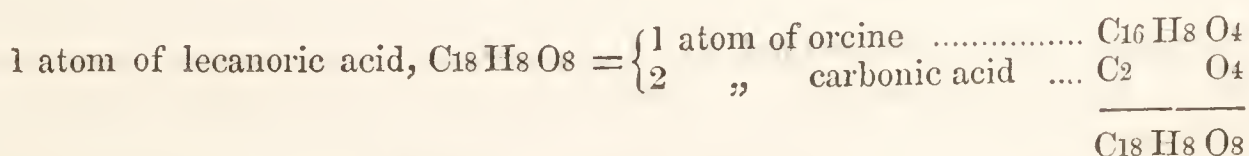
These substances are prepared from various *lichens*, amongst which, *Roccella tinctoria*, and *corallina*, *Lecanora Tartarea*, *Variolaria lactea*, and *dealbata*, have been especially resorted to. These lichens are principally collected on the rocks adjoining the sea, and there is a general similarity in the mode of treating them for the manufacture of the above-mentioned colors. They are cleaned, and ground into a pulp with water; ammoniacal liquors, derived chiefly from gas-works, or occasionally from urine, are from time to time added, and the mass is frequently stirred so as to expose it as much as possible to the action of air. Peculiar substances existing in the lichens are, during this process, so changed by the joint action of air, water, and ammonia, as to generate the coloring matter, which, when perfect, is pressed out, and chalk, plaster of Paris,



and occasionally some other substances, are added, so as to form it into a consistent paste. In this state it is of a purple or violet-red tint, and constitutes the *archil* of commerce, frequently called *Cudbear*, (from Cuthbert, one of the manufacturers of the article at Leith); it is the *orseille* and *persio* of the French and Germans. The other variety, called *litmus*, or in France and Germany, *tournesol* and *lacmus*, is generally made up into small cubes, and has a fine violet color\*. The lichens which are fit for the manufacture of these colors may be distinguished by moistening a sample of them with a little solution of ammonia, and setting it aside in a corked phial; if of the proper kind, the lichen and the liquor acquire a purple tint in the course of a few days.

The nature of the colorific principles of these lichens has been the subject of several analytical investigations, amongst which, those of Robiquet, (*Ann. Ch. et Ph.*, xlii. 236, and xlviii. 520,) of Heeren, (*Schweigger's Journ.*, lix. 313,) of Dumas, (*Chim. app. aux Arts*, viii. 40,) of Kane, (*Phil. Trans.*, 1840, p. 273, and *Ann Ch. et Ph.*, 3ème Sér., ii. 1 and 129,) and of Schunck, (*Ann. der Pharm.*, xli. 157, and *Mem. Chem. Soc.*, iii. 144,) are the most important. The following substances seem to have been discovered in them.

1. *Lecanorine*. *Lecanoric Acid*.  $C_{18}H_8O_8 + HO$ . This compound exists in different species of *lecanora*, and according to Rochleder and Heldt, in *Parmelia* (*Evernia*) *prunastri*. It is obtained by exhausting the lichen with ether, which is then distilled off, and leaves a residue containing lecanoric acid, mixed with resinous and fatty matter, and some substances soluble in water. The lecanoric acid not being very soluble in ether, the resin and fatty matter may be abstracted by the careful application of small portions of that solvent; the substances soluble in water are then washed out, and what remains is dissolved in a small quantity of boiling alcohol, from which the lecanoric acid crystallizes on cooling. Lecanoric acid may be extracted from the *Parmelia* by digesting it for some hours in a mixture of ammonia and alcohol, out of contact of air in a well-closed vessel; the clear liquor is then slightly supersaturated by acetic acid, and diluted with a third of its volume of water, when lecanoric acid is thrown down. The precipitate, after having beenedulcorated with a little water, is dried at  $212^{\circ}$ , dissolved in boiling alcohol, and set aside to crystallize. To obtain it perfectly pure, it is often necessary to redissolve in ether, and recrystallize, when rocellic acid, if any were present, remains undissolved. Lecanoric acid forms inodorous and tasteless stellated groups of silky acicular crystals, insoluble in water, but soluble in hot alcohol and ether. Subjected to dry distillation, it is resolved into *orcine* and carbonic acid; and it undergoes the same change when moistened with sulphuric acid and left in a damp place; or when boiled in solution of ammonia or potassa.



\* An article known in France under the name of *Tournesol en Drapeaux* and *Tournesol de Provence*, is derived from the juice of *Chrozophora tinctoria* (*Croton tinctorium*: LINN.;) an *Euphorbiaceous* plant: its manufacture is described by Joly, *Ann. Ch. et Ph.*, 3ème Sér., vi. 111.



The components of lecanoric acid, when rendered *anhydrous* by drying at 212°, are

|                          |    |      |     |      |        | Schunck.   | Rochleder<br>and Heldt. |
|--------------------------|----|------|-----|------|--------|------------|-------------------------|
| Carbon.....              | 18 | .... | 108 | .... | 60.00  | .... 60.76 | .... 60.22              |
| Hydrogen .....           | 8  | .... | 8   | .... | 4.44   | .... 4.45  | .... 4.79               |
| Oxygen .....             | 8  | .... | 64  | .... | 35.56  | .... 34.79 | .... 34.99              |
| <hr/>                    |    |      |     |      |        |            |                         |
| Anhydrous lecanoric acid | 1  |      | 180 |      | 100.00 | 100.00     | 100.00                  |

*Lecanorates.* Lecanoric acid expels carbonic acid from the alkaline carbonates, and forms soluble salts with their bases, which, however, on account of their extreme proneness to decomposition, have not been obtained in a solid state. When their recent and undecomposed solution is mixed with an acid, the lecanoric acid is separated in the form of a gelatinous precipitate. The aqueous solutions of the lecanorates of the alkaline earths, are precipitated by alcohol, which throws down the salt, and which may be boiled in alcohol without change. When a little perchloride of iron is added to an alcoholic solution of lecanoric acid, the liquor assumes a purple color, and water throws down a pale purple *lecanorate of iron*. When a solution of the acid is added to an alcoholic solution of acetate of lead, no precipitate ensues till the liquor is boiled, when *lecanorate of lead* falls, = Pb O, C<sub>18</sub> H<sub>8</sub> O<sub>8</sub>. When alcoholic solutions of acetate of copper and of lecanoric acid are mixed, no immediate change ensues, but after a time an apple-green *lecanorate of copper* falls. The alcoholic solution of lecanoric acid produces no precipitate in aqueous solutions of corrosive sublimate, nitrate of silver, or chloride of gold; but when an alkaline lecanorate is heated with the solutions of silver or of gold, the metals are reduced. When an alcoholic solution of lecanoric acid is subjected to the action of oil of vitriol, or of hydrochloric gas, *Lecanoric ether*, (*lecanorate of oxide of ethyle*, or Heeren's *pseudoerythrine*) is formed.

2. *Orcine*. C<sub>16</sub> H<sub>8</sub> O<sub>4</sub> + HO. This substance was discovered by Robiquet in his examination of *Variolaria dealbata*, and is one of the principal sources of the coloring matter derived from lichens. It is found ready formed in *Lichen roccella*, *parellus*, *deustus*, *tartareus*, *dealbatus*, &c., and is produced, as already stated, in various ways, from lecanorine. It is obtained by exhausting the dried and pulverised lichen in boiling alcohol, and filtering while hot; the liquor, as it cools, deposits a crystalline flocculent matter, which is to be separated; the alcohol is then to be distilled off, the residue evaporated to the consistency of extract, and this extract rubbed in a mortar with water so as to abstract the whole of its soluble matter. This aqueous solution is then evaporated to the consistence of syrup, and placed in a cold situation, where after some days it deposits long brown brittle needles, which are to be freed from the mother-liquor, redissolved in water, treated with animal charcoal, filtered, and again crystallized. These crystals are still yellow, and may be further purified by dissolving them in water, adding basic acetate of lead to the solution, decomposing the precipitate which is thrown down, by sulphuretted hydrogen, filtering, and crystallizing.

Orcine crystallizes in flat four-sided prisms, with dihedral summits; it has a sweet but somewhat repulsive taste, and it is perfectly neutral.

When dried at  $212^{\circ}$ , it loses a portion of its water of crystallization; at about  $550^{\circ}$  it rises in vapor, and may be distilled, and condensed in crystals which contain 1 atom of water: the density of its vapor is 5.7. (DUMAS.) It is soluble in water and in alcohol. *Anhydrous orcine* consists, according to the analysis of its compound with oxide of lead, of

|                   |    |     |     |     |        |
|-------------------|----|-----|-----|-----|--------|
| Carbon.....       | 16 | ... | 96  | ... | 70·59  |
| Hydrogen .....    | 8  | ... | 8   | ... | 5·88   |
| Oxygen .....      | 4  | ... | 32  | ... | 23·53  |
| <hr/>             |    |     |     |     |        |
| Anhydrous oricine | 1  |     | 136 |     | 100·00 |

*Sublimed orcine* is composed of

| Dumas. Schunck.    |   |       |                                   |        |        |     |     |       |  |
|--------------------|---|-------|-----------------------------------|--------|--------|-----|-----|-------|--|
| Carbon             | ....16....96....66·21....67·78....67·76 | } = { | Anhydrous<br>orcine<br>Water..... | 1      | ...    | 136 | ... | 93·79 |  |
| Hydrogen           | 9.... 9.... 6·20.... 6·50.... 6·60      |       |                                   |        |        |     |     |       |  |
| Oxygen             | .... 5....40....27·59....28·72....25·64 |       |                                   |        |        |     |     |       |  |
| <hr/>              |   |       |                                   |        |        |     |     |       |  |
| Sublimed<br>orcine | } 1                                     | 145   | 100·00                            | 100·00 | 100·00 |     |     |       |  |
|                    |   |       |                                   |        |        |     |     |       |  |
|                    | 1                                       | 145   | 100·00                            | 100·00 | 100·00 |     |     |       |  |

And *crystallized orcine* (from aqueous solution) consists of

| Dumas. Will. Schunck.  |        |        |           |           |           |        |        |                                   |        |          |        |
|------------------------|--------|--------|-----------|-----------|-----------|--------|--------|-----------------------------------|--------|----------|--------|
| Carbon .....           | 16.... | 96.... | 58·89.... | 58·35.... | 58·46.... | 58·98  | } = {  | Anhy-<br>drous<br>orcine<br>Water | 1 .... | 136 .... | 83·45  |
| Hydrogen ....          | 11.... | 11.... | 6·75....  | 6·98....  | 6·75....  | 7·06   |        |                                   |        |          |        |
| Oxygen .....           | 7....  | 56.... | 34·36.... | 34·67.... | 34·79.... | 33·96  |        |                                   |        |          |        |
| <hr/>                  |        |        |           |           |           |        |        |                                   |        |          |        |
| Crystallized<br>orcine | }      | 1      | 163       | 100·00    | 100·00    | 100·00 | 100·00 |                                   | 1      | 163      | 100·00 |
|                        |        |        |           |           |           |        |        |                                   |        |          |        |

The aqueous solution of orcline gives a white precipitate with basic acetate of lead, to which Schunck assigns the formula  $5\text{Pb O}, + \text{C}_{16} \text{H}_9 \text{O}_5$ . Dumas obtained it by adding nitrate of lead to excess of a hot solution of orcline mixed with ammonia; the precipitate, washed with hot water, and dried at  $300^\circ$ , consisted of

|               |       |     |       |     |        |        |
|---------------|-------|-----|-------|-----|--------|--------|
|               |       |     |       |     |        | Dumas. |
| Carbon .....  | 16    | ... | 96    | ... | 13·79  | 15·15  |
| Hydrogen ...  | 8     | ... | 8     | ... | 1·15   | 1·11   |
| Oxygen .....  | 4     | ... | 32    | ... | 4·59   | 3·40   |
| Oxide of lead | 5     | ... | 560   | ... | 80·47  | 80·34  |
|               | <hr/> |     | <hr/> |     | <hr/>  | <hr/>  |
|               | 1     |     | 696   |     | 100·00 | 100·00 |

When oricine is exposed to air it gradually reddens, especially when the sun occasionally shines upon it. When subjected to the action of chlorine it heats, fuses, and hydrochloric acid is produced; when no further action ensues, a crystalline compound results, which has been termed *Chlororcéic acid*. Nitric acid acts upon oricine with the evolution of nitrous gas, and a red solution is formed, which deposits a resin-like substance; when the action of the acid is continued, the resin is redissolved, forming a bright yellow solution, which deposits crystals of oxalic acid. The fixed alkalis convert oricine into a brown substance, which has not been examined. Gaseous ammonia is absorbed by oricine, and on exposure to air it again escapes; but when water is present the



oxygen of the atmosphere is absorbed, and a colored azotised body is the result, to which the name of *orcéine* or *orcéic acid* has been given.

3. *Orcéine. Orcéic Acid.*  $C_{16}H_8O_6N, +HO$ . This substance is best obtained by placing pulverised orceine in a capsule, together with a saucer of solution of ammonia, under a bell-glass; the orceine becomes brown, but on exposure to air the excess of ammonia escapes, and on adding a little water, and a few drops of ammonia, a purple solution is obtained, from which acetic acid throws down *orcéine*, or, as Berzelius terms it, *orcéic acid*. Sulphuretted hydrogen decolors the purple liquor, not by deoxidizement, but by entering into combination with the *orcéic acid*, for the color reappears on saturating the sulphuretted hydrogen by an alkali. Robiquet observed, that although *orcéic acid* yielded ammonia by dry distillation, none was evolved on heating it in solution of caustic potassa; whence he concluded, that the nitrogen constituted one of its elements, and was not present in the form of ammonia. Liebig, however, asserts that when *orcéic acid* is boiled in potassa, ammonia is evolved; but this by no means proves the presence of *ammonia* in the *orcéic acid*. When *orcéic acid* is boiled in a weak solution of ammonia till all free ammonia is expelled, and nitrate of silver added to the resulting purple liquor, a dark violet-colored precipitate falls, which is an *orcéate of silver*, having, according to Dumas, the formula  $2AgO + C_{16}H_8O_6N$ . The composition of *anhydrous orcéic acid*, deduced from the analysis of this silver salt, is

|                                    |    |     |     |     |        |
|------------------------------------|----|-----|-----|-----|--------|
| Carbon .....                       | 16 | ... | 96  | ... | 57.83  |
| Hydrogen .....                     | 8  | ... | 8   | ... | 4.82   |
| Oxygen .....                       | 6  | ... | 48  | ... | 28.92  |
| Nitrogen .....                     | 1  | ... | 14  | ... | 8.43   |
| <hr/>                              |    |     |     |     |        |
| Anhydrous <i>orcéic acid</i> ..... | 1  |     | 166 |     | 100.00 |

The *crystallized*, or *hydrated acid*, appears to contain an atom of water; its components therefore are

|                             |        |     |        |       |       |
|-----------------------------|--------|-----|--------|-------|-------|
|                             | Dumas. |     |        |       |       |
| Carbon.....                 | 16     | 96  | 54.86  | 55.3  | } = { |
| Hydrogen .....              | 9      | 9   | 5.14   | 5.0   |       |
| Oxygen .....                | 7      | 56  | 32.00  | 31.8  |       |
| Nitrogen .....              | 1      | 14  | 8.00   | 7.9   |       |
| <hr/>                       |        |     |        |       | } = { |
| Hydrated <i>orcéic acid</i> | 1      | 175 | 100.00 | 100.0 |       |
|                             |        |     |        |       | } = { |
|                             |        |     |        |       |       |

It appears probable that in the conversion of orceine into *orcéic acid*, under the above mentioned influence of ammonia, 1 atom of anhydrous orceine combines with 5 atoms of oxygen and with the elements of 1 atom of ammonia, to produce 1 atom of anhydrous *orcéic acid* and 3 atoms of water.

|                        |                |       |                              |                 |
|------------------------|----------------|-------|------------------------------|-----------------|
| 1 atom of orceine .... | $C_{16}H_8O_4$ | } = { | 1 atom of <i>orcéic acid</i> | $C_{16}H_8O_6N$ |
| 1 „ ammonia            | $H_3N$         |       |                              |                 |
| 5 „ oxygen....         | $O_5$          |       | 3 „ water.....               | $H_3O_3$        |
| <hr/>                  |                |       | <hr/>                        |                 |
| $C_{16}H_{11}O_9N$     |                |       | $C_{16}H_{11}O_9N$           |                 |

The salts of the *orcéic acid* are all of a fine deep red or purple color;



its combinations with the alkalis are soluble in water, and are decomposed by acids, which precipitate orcéic acid. The compounds with the earths and other oxides are chiefly insoluble.

It will be obvious that in the preparation of blues from lichens, orcéic acid is produced under the influence of ammonia. It is not itself a permanent dye-stuff, but is a valuable auxiliary in the production of other blues and purples.

4. *Erythrine*. (HEEREN.)' *Erythryline*. (KANE.) *Erythric Acid*. (SCHUNCK.) These substances are probably identical with, or at all events, closely related to lecanorine; they have been described at length by Kane, according to whom, two coloring matters are contained in archil, which he describes as oxides of a common radical, and as derived from erythrine under the influence of oxygen and of ammonia; one of these coloring matters he terms *alpha-orcéine*,  $=\text{C}_{18}\text{H}_{10}\text{O}_5\text{N}$ ; and the other *beta-orcéine*,  $=\text{C}_{18}\text{H}_{10}\text{O}_8\text{N}$ ; their properties, he says, are *identical*. By further oxidizement they pass into *azolitmine*,  $=\text{C}_{18}\text{H}_{10}\text{O}_{10}\text{N}$ , which he represents as forming the greater part of the coloring matter of litmus. A very compendious account of Kane's views respecting the coloring matters derived from the lichens, will be found in his *Elements of Chemistry*, p. 1048. Schunck assigns the formula  $\text{C}_{34}\text{H}_{19}\text{O}_{15}$ , to his *crystallized erythric acid*; and  $\text{C}_{34}\text{H}_{15}\text{O}_{11}$ , to the acid in combination with oxide of lead.

An important use of litmus has been frequently mentioned, namely, for the preparation of *litmus paper*. "In preparing litmus paper, an infusion is made of commercial litmus, filtered, concentrated by a water-bath, and a very small quantity of carbonate of soda added. Good letter paper cut into slips of three inches in breadth, is dipped into the infusion, allowed to dry, and the dipping repeated; or the infusion may be applied to one side only of thin and sized drawing paper. For *red test paper*, the infusion of litmus is acidulated slightly by means of acetic acid. A paper prepared from an infusion of the best cudbear, without the addition of either alkali or acid, has a purple color, and is affected both by acids and alkalis: it is convenient in *alkalimetry*, being already too red to be affected by carbonic acid, while it is distinctly reddened by the mineral acids." (GRAHAM. For more explicit directions upon the subject of *test-papers*, and their uses, see FARADAY's *Chemical Manipulation*, § xii.) Litmus was the coloring matter formerly used for tinging the spirit in thermometer tubes, but was very liable to fade. The Abbé Nollet observes, (in the *French Memoirs* for the year 1742,) that the *colorless* spirit, upon breaking the tube, soon resumes its color, and this for a number of times successively; that a watery tincture of archil, included in the tubes of thermometers, lost its color in three days; and that in an open deep vessel, it became colorless at bottom, while the upper part retained its color. A solution of archil in water, applied on cold marble, stains it of a beautiful violet or purplish-blue, far more durable than the color which it communicates to other bodies. M. du Fay says, he has seen pieces of marble stained with it, which in two years had suffered no sensible change. It sinks deep into the marble, sometimes above an inch, and at the same time spreads upon the surface, unless the edges be bounded by wax or some similar substance: it is said to make the marble somewhat more brittle.



The preceding are the principal substances which have been distinctly identified as connected with the *coloring powers* of lichens: lichens also contain *fatty acids*, and *bitter principles*, which will be noticed in reference to their general analysis, the results of which are given in the alphabetical list of plants, under the head of "Chemical Botany." A number of other proximate principles have been stated to exist in, or to be derived from certain species of *lichens*, and some of them seem, under the influence of air and other agents, to produce coloring matter; but neither their composition nor their distinctive characters have been sufficiently accurately determined, to justify their being placed among those definite colorific principles to which this curious class of vegetable products owes its importance in the arts.

### III. MADDER.

The plant which furnishes this valuable dye-stuff (*Rubia tinctorum*) is common in the south of Europe and in many parts of the Levant, and is largely cultivated in Holland; it grows to about three feet in height, and has a long spreading fibrous root, which is the part used in dyeing: it is carefully dried, cleaned, and ground into a coarse powder, which is of a dingy-red or orange color, and very apt to be deteriorated by moisture. The Levantine madder, called *ligari*, *allizari*, and *azale*, has a finer color than the Dutch, but the latter is more carefully prepared and dried.

Although madder has been examined by many able chemists, the nature of its coloring principles is as yet but imperfectly understood. According to Berzelius (*Lehrbuch*), and Runge (*R. D. Thomson's Records of Science*, and *Ann. Ch. et Ph.*, lxiii. 282), madder-root contains no less than five modifications of coloring matter—namely, a purple, red, orange, yellow, and brown; it is, however, highly probable that these are modifications of, or derivatives from some original principle, inasmuch as the red color is not pre-existent in the madder, but appears to be the product of the action of oxygen upon a yellow substance. Kühlmann (*Ann. Ch. et Ph.*, xxiv. 425); Colin and Robiquet (*Ibid.*, xxxiv. 225); Zennek (*Quart. Journ.*, N. S., v. 198, and *Poggend. Ann.*, xiii. 261); Gaultier de Claubry and Persoz (*Ann. Ch. et Ph.*, xlviii. 69); and Schlumberger (*Bulletin of the Industrial Society of Mülhausen*), are the other principal authorities upon this subject.

*Madder-purple* is obtained by repeatedly boiling the previously well-washed root in a strong solution of alum, and filtering whilst hot. On cooling, a brownish-red substance falls, which is chiefly *madder-red*, and which is separated by decantation. Sulphuric acid is then added to the clear liquor, which throws down the *madder-purple*, but some days are required before the whole of it separates; it is then collected, boiled with hydrochloric acid to separate alumina, and lastly digested in alcohol; from this tincture the greater part of the alcohol may be distilled off, and the residue, submitted to spontaneous evaporation, deposits the so-called *purple* in the form of a crystalline powder. It is itself of an orange-red tint, but furnishes a deep rose-colored solution with water: its solution in alcohol and in ether is deep red or purple; it fuses when heated, and at a higher temperature is partly decomposed, and partly

volatilized. Acids render it yellow, and when boiled in dilute acids it is dissolved, but again deposited as an orange-colored flocculent precipitate on cooling. With alkalis it forms a deep-red solution. When its solutions are boiled with chalk, the whole of the coloring matter is abstracted from the liquor.

*Madder-red* constitutes the principal part of the aluminous precipitate above mentioned. To separate it, the precipitate is first boiled in dilute hydrochloric acid, and then dissolved in alcohol. This alcoholic solution is mixed with a concentrated solution of alum, and heated to its boiling-point, when the *madder-red* is thrown down (a portion of the purple being retained in solution.) To purify it, it is dissolved in ether, and on evaporation it remains in the form of a yellow-brown crystalline powder, which gives a dark-yellow solution with boiling water, and falls again as the liquor cools. It dissolves in alcohol and in ether with a reddish-yellow color. When heated it rises in vapor, which condenses in orange-colored silky needles. Acids render it yellow; its ammoniacal solution is purple, and with solution of caustic potassa it forms a violet liquor. When boiled with water and chalk a dark purple, and with hydrate of lime a violet-blue solution is obtained.

*Madder-orange* is obtained by digesting the washed root for 16 hours in 8 parts of water at 60°, and straining the infusion through muslin; it gradually deposits small crystals, which are to be collected, dried, and dissolved in boiling alcohol; on cooling, it deposits the *madder-orange*, which is to be washed with cold alcohol till the washings are no longer reddened by sulphuric acid. It then forms an orange-yellow powder, which when dissolved in boiling water or boiling alcohol, separates in yellow flocks on cooling. Ether is its best solvent. It is fusible, and when highly heated, produces a yellow vapor, and leaves carbon. Its solution in caustic potassa is deep rose-red, and in ammonia reddish-brown. It combines, like madder-purple, with chalk.

These three coloring matters, either singly or combined, produce the different tints which, in dyeing and calico-printing, are obtained from madder.

*Madder-yellow*. *Xanthine* (of Köhlmann). When a cold infusion of madder-root is mixed with its bulk of lime-water, a dark-red precipitate falls, which, digested in acetic acid, yields a solution containing acetate of lime and *madder-yellow*; the other coloring matters are also to a small extent thus dissolved, but they may be separated by means of wool which has been mordanted with alum; the solution is then evaporated, and the residue dissolved in alcohol. This alcoholic solution is mixed with a solution of acetate of lead in alcohol, and the scarlet precipitate thus produced is diffused in water, and decomposed by sulphuretted hydrogen: on evaporating the filtered liquor, the *madder-yellow* remains in the form of an extract.

*Madder-brown* is represented as a dark-colored substance, insoluble in water and in alcohol, and inapplicable to the purposes of dyeing; it is soluble in the alkalis, and precipitated from these solutions by the acids.

Two *acids* have been described as existing in madder, but they have been very imperfectly examined, and as yet possess neither technical nor scientific interest.



*Alizarine*, *Purpurine*, *Garancine*, are terms which have been applied to the madder-red and madder-purple, above described, or at least to their sublimed products. *Alizarine* has been represented as  $= C_{37}H_{12}O_{10}$ , and is obtained, according to Robiquet and Colin, as follows: ground madder is gradually added to its weight of oil of vitriol so as to prevent increase of temperature, by which, in the course of two or three days, every thing but the alizarine is more or less charred and destroyed. The acid is then washed out of the black mass, which is dried, and digested in cold alcohol to remove fatty matter; it is then boiled in alcohol to abstract the alizarine; when the alcohol is distilled off from this solution, the alizarine falls, and may be collected upon a filter, washed, dried, and carefully sublimed; it forms delicate needles of an orange color, but unless the subliming vessel is very low and flat, the greater part of it is decomposed by the application of the necessary heat. They describe alizarine as very sparingly soluble in boiling water, to which it imparts a rose tint. At  $54^{\circ}$  it dissolves in 212 parts of alcohol, and in 160 parts of ether. It is soluble in albumen, and remains in combination with it when coagulated.

When madder is mixed with the food of animals their bones gradually become tinged by it, and in this way, in a growing animal, alternate layers of white and red bone may be formed: the coloring matter also passes off by the urine, which, on the addition of ammonia, yields a precipitate of red phosphate of lime.

Madder is amongst the most important and permanent of the red dyes, and many of the most beautiful tints are obtained from it, especially stable reds and purples; among them, the most remarkable are those termed *Adrianople* or *Turkey reds*, which are produced by a series of complicated operations, the rationale of which is but imperfectly understood. (See, in reference to this subject, DUMAS's *Chimie App. aux Arts*, viii., and URE's *Dictionary*, art. *Madder*.)

#### IV. CARTHAMINE. CARTHAMEINE.

This is the coloring principle of *Safflower*, the petals of the *Carthamus tinctorius* or *Bastard saffron*. It is cultivated in Spain, and in many parts of the Levant, whence it is chiefly imported, but on account of its price it is seldom used, except to give the finishing hue to some silks, and in the preparation of the article called *rouge*.

Safflower contains a *red* coloring-matter which is insoluble in water, and a *yellow* soluble substance. The former has been distinguished as *carthaméine*, and appears to be derived from the oxidation of a peculiar principle existing in the petals, which has been called *carthamine*. (PREISSER, *Erdmann and Marchand's Journ.*, xxxii. 141.)

*Carthamine* (*Carthamous acid* of Dumas) is obtained from the flowers, after all soluble matters have been extracted by water, by digesting them in a weak solution of carbonate of soda, and precipitating the alkaline liquor by hydrated oxide of lead: the precipitate is diffused through water, and decomposed by excess of sulphuretted hydrogen, and the solution filtered from the sulphuret of lead is then left to spontaneous evaporation. The carthamine crystallizes in small white prismatic needles of a bitterish taste, very little soluble in water, but somewhat more so in

alcohol; it is not volatile, but fuses when heated, exhales a pungent odor, and burns away without residue; exposed to the air, it gradually acquires a yellow color. It is decomposed by concentrated sulphuric acid, but dissolves in the dilute acid, and also in warm hydrochloric and nitric acid.

When the alkaline solution of carthamine is left in contact of oxygen, it becomes first yellow, and then red, and on saturating this red liquor with citric acid, red *carthaméine* is thrown down. When air is excluded, the alkaline solution remains colorless. Acetate of lead occasions a white precipitate in solution of carthamine, which, on exposure, first becomes yellow, and then red. The formula assigned by Preisser to *crystallized carthamine* is  $C_{26}H_9O_5 + 2HO$ . The water of crystallization is expelled by heat, and the *anhydrous* substance then yields, on analysis,

|                      |    |      |     |      | Preisser. |            |
|----------------------|----|------|-----|------|-----------|------------|
| Carbon .....         | 26 | .... | 156 | .... | 76.09     | .... 76.31 |
| Hydrogen .....       | 9  | .... | 9   | .... | 4.39      | .... 4.28  |
| Oxygen .....         | 5  | .... | 40  | .... | 19.52     | .... 19.41 |
| <hr/>                |    |      |     |      |           |            |
| Anhydrous carthamine | 1  |      | 205 |      | 100.00    | 100.00     |

*Carthaméine. Carthamic Acid.* This is the product of the oxidization of carthamine, under the influence of alkaline bases: it exists in the safflower, from which it may be extracted by digesting it, after the yellow matter has been removed by water, in a solution of carbonate of soda, and then precipitating by citric acid. It forms a dark-red powder, insoluble in water and in acids, and very sparingly soluble in alcohol, to which it communicates a fine red color: it is also sparingly soluble in ether. It is not volatile, but decomposed by dry distillation. It forms salts with the alkalis, from which it is thrown down by the organic acids of a bright rose-red. It has the formula  $C_{26}H_9O_7$ , being composed, according to Preisser, of

|                       |    |      |     |      | Preisser. |            |
|-----------------------|----|------|-----|------|-----------|------------|
| Carbon .....          | 26 | .... | 156 | .... | 70.59     | .... 70.50 |
| Hydrogen .....        | 9  | .... | 9   | .... | 4.07      | .... 4.08  |
| Oxygen .....          | 7  | .... | 56  | .... | 25.34     | .... 25.42 |
| <hr/>                 |    |      |     |      |           |            |
| Carthamic acid ... .. | 1  |      | 221 |      | 100.00    | 100.00     |

When the *yellow* aqueous infusion of safflower is evaporated, it leaves an extract very soluble in water and easily putrescible; it is precipitated by the acids, and soluble in the alkalis. With acetate of lead, it produces an orange-yellow precipitate; green, with sulphate of copper; and yellow with chloride of tin. It is not rendered red by oxidizing agents.

The affinity of carthaméine for cotton and silk is such, that when it is recently precipitated, those substances immediately combine with it and become at first rose-colored, and afterwards of a fine red, so that they may be thus dyed without the intervention of a mordant; the stuffs so dyed, are rendered yellow by the alkalis, and the color is, to a certain extent, restored by the acids. Carthaméine is never used in dyeing wool. When it is precipitated from concentrated solutions, it furnishes a liquid paint, which evaporated upon saucers, leaves a residue of somewhat metallic lustre, used as a pink dye-stuff, and which, mixed with finely powdered talc, and dried, constitutes common *rouge*.



V. HÆMATOXYLINE. HÆMATEINE.

These substances are extracted from *logwood*, a dye-stuff of considerable importance: it is the heartwood of the *Hæmatoxylon Campechianum*, and is imported from Campeachy, Honduras, and Jamaica, in hard and dense logs, about three feet long, and of a dark-red or purple color. It was first chemically examined by Chevreul (*Annales de Chimie*, LXXXI. 158, and LXXXIII. 53), and has been more lately experimented upon by Erdmann (*Erdmann and Marchand's Journ.*, xxvi. 183. Löwig, *Chem. d. Org. verbind.*, i. 862.) In the dye-house it is used for the production of certain *reds* and *blues*, but its chief consumption is for *blacks*, which are obtained of various intensities, by means of iron and alum bases.

*Hæmatoxyline* (*Hématine* of Chevreul,) is best obtained, according to Erdmann, by pulverising the watery extract of the wood as prepared for pharmaceutical use, mixing it with a portion of sand to prevent agglutination, and digesting the mixture with 6 or 8 times its volume of ether; it should be frequently shaken, and after a few days the clear brown tincture should be poured off, and the greater part of the ether distilled from it; the residue is then mixed with water, and left to spontaneous evaporation in a lightly-covered basin. After some days the hæmatoxyline crystallizes, and may be washed with cold water, and pressed between folds of bibulous paper to free it from the mother-liquor. From 2 lbs. of extract digested in 10 lbs. of ether, Erdmann obtained 4 ounces of hæmatoxyline. Chevreul digests the extract in alcohol, and leaves the tincture to spontaneous evaporation, washing the mother-liquor from the crystallized product, with cold alcohol.

*Hæmatoxyline* forms transparent brownish-yellow prismatic crystals, which yield a pale yellow powder; they are efflorescent, and in a dry air lose the greater part of their water of crystallization. When rapidly heated to 212° they fuse, and then gradually become anhydrous. Hæmatoxyline has a sweet taste resembling that of liquorice root, without either bitterness or astringency. It is very sparingly soluble in cold water, but boiling water readily dissolves it, and on cooling deposits it in crystals, which, under ordinary circumstances, contain 8 atoms of water of crystallization; but if a concentrated hot solution be allowed to cool in a well-closed vessel, it forms pale-yellow granular crystals, which only include 3 atoms of water. With alcohol and ether hæmatoxyline produces reddish-yellow solutions.

Hæmatoxyline has been analyzed by Erdmann; in its *anhydrous* state, it is C<sub>40</sub> H<sub>17</sub> O<sub>15</sub>;

|                        |    |      |     |      |        |            |
|------------------------|----|------|-----|------|--------|------------|
|                        |    |      |     |      |        | Erdmann.   |
| Carbon .....           | 40 | .... | 240 | .... | 63·66  | .... 63·19 |
| Hydrogen .....         | 17 | .... | 17  | .... | 4·50   | .... 4·65  |
| Oxygen .....           | 15 | .... | 120 | .... | 31·84  | .... 32·16 |
| <hr/>                  |    |      |     |      |        |            |
| Anhydrous hæmatoxyline | 1  |      | 377 |      | 100·00 | 100·00     |

The ordinary crystals are C<sub>40</sub> H<sub>17</sub> O<sub>15</sub> + 8HO; their ultimate elements being





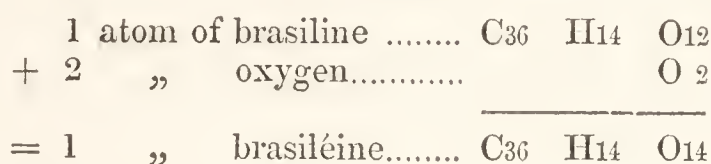
little fresh ammonia being from time to time added, so as to maintain it in very slight excess, granular crystals of hæmatéine are formed in the course of a few days: these must be washed with cold water, dried by pressure in absorbent paper, dissolved in water, and precipitated by acetic acid.

Thus purified, hæmatéine forms a reddish-brown precipitate, which, when dried, becomes dark-green and of a metallic hue. It forms a brown solution in hot water, which, when rapidly evaporated, gives a succession of greenish crystalline pellicles, and on cooling deposits the hæmatéine either in a granular or gelatinous form. The ultimate components of these crystals are,

|                               |    |     |        |         | Erdmann. |                        |             |     |       |      |  |
|-------------------------------|----|-----|--------|---------|----------|------------------------|-------------|-----|-------|------|--|
| Carbon .....                  | 40 | 240 | 62.66  | 62.799  | } = {    | Anhydrous<br>hæmatéine | 1           | 374 | 97.65 |      |  |
| Hydrogen ....                 | 15 | 15  | 3.91   | 4.135   |          |                        |             |     |       |      |  |
| Oxygen .....                  | 16 | 128 | 33.43  | 33.066  |          |                        |             |     |       |      |  |
| <hr/>                         |    |     |        |         |          | {                      | Water ..... | 1   | 9     | 2.35 |  |
| Crystallized }<br>hæmatéine } | 1  | 383 | 100.00 | 100.000 | <hr/>    |                        |             |     |       |      |  |
| <hr/>                         |    |     |        |         |          |                        | <hr/>       |     |       |      |  |
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|-----------------|----|------|-----|------|--------|------|---------------------|
| Carbon .....    | 36 | .... | 216 | .... | 66.25  | .... | Preisser.<br>65.498 |
| Hydrogen .....  | 14 | .... | 14  | .... | 4.29   | .... | 4.324               |
| Oxygen .....    | 12 | .... | 96  | .... | 29.46  | .... | 30.178              |
| <hr/>           |    |      |     |      |        |      |                     |
| Brasiline ..... | 1  |      | 326 |      | 100.00 |      | 100.000             |

When an aqueous solution of brasiline is exposed to air, it gradually acquires a yellow and then a red tint; but if it be boiled, it immediately becomes of a crimson-red, and deposits, during evaporation, crystals of *brasiléine*: this change is represented by Preisser as follows:



Dilute nitric acid gives a fine red tint to a solution of brasiline, and on evaporation oxalic acid is formed. Brasiline yields formic acid when distilled with peroxide of manganese and sulphuric acid, or with chromic acid. It reduces nitrate of silver and chloride of gold. The sulphuric solution of brasiline soon blackens; and the hydrochloric solution reddens on exposure to air. When crystals of brasiline are placed under a bell-glass near a saucer containing ammonia, they are rendered purple, but not unless air be at the same time present. The solution of brasiline is reddened by potassa and soda, and by lime water, air being present. When a colorless solution of brasiline is agitated with oxide of lead, a compound is obtained,  $=\text{PbO}, \text{C}_{36} \text{H}_{14} \text{O}_{12}$ . (PREISSER.)

*Brasiléine* was originally obtained by Chevreul by dissolving an aqueous extract of the wood in water, and agitating the solution with oxide of lead; the liquor was then poured off the deposit, evaporated to dryness, and the residue digested in alcohol; the alcoholic solution was then filtered and evaporated, and the residue dissolved in water, to which a solution of glue was added to throw down tannine; it was then filtered, evaporated, and the residue digested in alcohol; this last alcoholic solution was filtered, and left the *brasiléine* on evaporation. (*Annales de Chimie*, LXVI. 325.) Preisser analysed *brasiléine* obtained by the oxidization of brasiline, and found it composed of

|                  |    |      |     |      |        |      |                     |
|------------------|----|------|-----|------|--------|------|---------------------|
| Carbon .....     | 36 | .... | 216 | .... | 63.16  | .... | Preisser.<br>63.324 |
| Hydrogen .....   | 14 | .... | 14  | .... | 4.09   | .... | 3.967               |
| Oxygen .....     | 14 | .... | 112 | .... | 32.75  | .... | 32.709              |
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| Brasiléine ..... | 1  |      | 342 |      | 100.00 |      | 100.000             |

*Brasiléine*, as obtained by Chevreul, forms very small orange-colored crystals, which produce a red solution in water, alcohol, and ether. On adding a little acid the color is changed to pale yellow. With sulphuric, nitric, and hydrochloric acid, it is a dirty yellow, but bright and permanent with phosphoric and citric acid. (BONSDORFF, *Schweigger's Journ.*, xxxv. 216 and 329.) The alkalis, and the salts of lead and of tin, change the aqueous solution of *brasiléine*, and paper tinged with it, to a purple color, and alum gives a red precipitate. Preisser analysed a compound of *brasiléine* with oxide of lead, and found it composed of  $\text{PbO}, \text{C}_{36} \text{H}_{14} \text{O}_{14}$ . (LÖWIG, *Chim. d. Org. verbind.*, i. 856.)



Sulphurous acid, hyposulphurous acid, and sulphuretted hydrogen, in the presence of water and of an acid, reduce brasiléine to brasiline.

Dr. Thomson observes that, within the last ten years, brazil wood has been nearly superseded by a wood imported from Africa, called by the dyers *cam wood*: it gives a finer and more permanent color than brazil wood: the tree which yields it grows in Sierra Leone, and the interior of Africa, and is figured in Loddiges' *Botanical Cabinet* under the name of *Baphia nitida*.

Brazil wood is distinguished from logwood by its paler color, and by the precipitates which it affords with acetate of lead, protochloride of tin, and lime water, which are crimson, instead of being violet-colored, as with logwood. Their infusions are both rendered yellow by a drop of sulphuric or hydrochloric acid.

Nicaragua and peach wood are also the produce of species of *Cæsalpinia*; their infusions are well adapted for extemporaneous illustrations of the art of dyeing and calico-printing. *Red ink* is usually made by boiling about two ounces of Brazil wood in a pint of water for a quarter of an hour, and adding a little gum and alum.

## VII. SANTALINE. SANTALÉINE.

*Red Sanders* is the name given in this country to the wood of the *Pterocarpus santalinus*, a large tree which grows upon the Coromandel coast, and in other parts of India, especially Ceylon. It was first chemically examined by Pelletier, in 1814, (*Journ. de Phys.*, lxxix. 268), who separated its coloring matter, under the name of *santaline*.

Preisser has given the name of *santaline* to a crystalline principle which is obtained by digesting the pulverised wood in ether, evaporating the tincture to about two-thirds of its bulk, and then digesting in it hydrated oxide of lead; the resulting precipitate is decomposed by sulphuretted hydrogen, and the filtered liquor evaporated *in vacuo*. (*Erdmann and Marchand's Journ.*, xxxii. 145.)

*Santaline* thus obtained is a white crystalline powder, which speedily reddens on exposure to air. It is instantly reddened by the alkalis, and furnishes red solutions with the greater number of the dilute acids. It dissolves in water, alcohol, and ether, and when its aqueous solution is long boiled under exposure to air, it is converted into santaléine.

*Santaléine*, when obtained by the oxidizement of santaline, is in the form of a dark-red crystalline powder. Its probable formula is  $C_{16}H_8O_3$ , but neither this nor the composition of santaline has been accurately determined. It may be extracted from the wood, either by alcohol, or by aqueous ammonia; in the former case it is obtained by the evaporation of the tincture; and in the latter, by precipitation by an acid. It is of a dark-red color, insipid, inodorous, and insoluble in water, but soluble in alcohol and in ether. The weak alcoholic solution is yellow; but the concentrated, red. The ethereal solution is yellow, and leaves a yellow residue when evaporated *in vacuo*; but if in the air, red santaléine remains; so that ether probably deoxidizes it. Santaléine is soluble in acetic acid, and, to a small extent in volatile oils, to which it gives a red color. The alcoholic solution of santaléine produces a dark violet color with persulphate of iron, a pale violet with the salts of lead, a purple

with solution of tin, a scarlet with corrosive sublimate, and a reddish-brown precipitate with nitrate of silver. Boiling alcohol extracts a portion of the coloring matter from all these precipitates.

VIII. ANCHUSINE. ANCHUSIC ACID.

These terms have been applied to the coloring-matter of the root of *Alkanet* (*Anchusa tinctoria*), a species of *bugloss*, which is a native of the warmer parts of Europe, and cultivated in our gardens; the greatest quantities are raised in Germany and France. Anchusine has been examined by John (*Chemische Schriften*, iv. 81), and by Pelletier. (*Ann. Ch. et Ph.*, Li. 182.) To obtain it, all soluble matters are in the first instance abstracted from the bruised root by water; it is then digested in a solution of carbonate of potassa, and from this alkaline solution the coloring-matter may be precipitated by an acid. Anchusine is also obtained by digesting the alcoholic extract of the root in ether, and evaporating the ethereal solution.

*Anchusine* has the characters of a resin; it is dark red, and of a resinous fracture, softened by heat, insoluble in water, soluble in alcohol, and very soluble in ether and in fat and volatile oils, to all which it communicates a bright red color. When the alcoholic or ethereal solution of anchusine is mixed with water and boiled, it gradually becomes brown. The red color in the first instance changes to blue-green, and a black substance remains on evaporation to dryness, soluble in water and in alcohol; the latter solution is reddened by chlorine: acids render it grey, and alkalis blue.

When anchusine is carefully heated, a part of it sublimes in the form of a violet-colored vapor, which condenses in a flocculent state; but the temperature at which it evaporates and that at which it is decomposed are so near each other, that a considerable portion of it is always lost in the operation. By the action of nitric acid, anchusine is converted into oxalic acid and a bitter substance. Sulphuric acid dissolves it without decomposition, and again deposits it when diluted. Hydrochloric acid has no action upon it. It is soluble in the alkalis, forming blue solutions, and on accurately saturating these with an acid, a blue precipitate falls, which is difficultly soluble in water, but soluble in ether; it is reddened by the acids. The alcoholic solution of anchusine is precipitated crimson-colored by protochloride of tin; blue by subacetate of lead; dark-violet by the salts of iron, and flesh-colored by corrosive sublimate; alum produces no precipitate.

According to Pelletier's analysis, the formula of anchusine is  $C_{17}H_{10}O_4$ , its components being

|                      |         |      |           |      |              |      | Pelletier.    |
|----------------------|---------|------|-----------|------|--------------|------|---------------|
| Carbon .....         | 17      | .... | 102       | .... | 70.83        | .... | 71.178        |
| Hydrogen.....        | 10      | .... | 10        | .... | 6.94         | .... | 6.826         |
| Oxygen.....          | 4       | .... | 32        | .... | 22.23        | .... | 21.996        |
| <hr/> Anchusine..... | <hr/> 1 |      | <hr/> 144 |      | <hr/> 100.00 |      | <hr/> 100.000 |



IX. LAC.

This is a resinoid substance, the secretion of which appears to depend upon the puncture of a small insect (the *Coccus ficus*), made for the purpose of depositing its ova, upon the branches of several plants, especially the *Ficus religiosa* and *indica*, the *Rhamnus jujuba*, the *Croton lacciferum*, and the *Butea frondosa*, which grow in Assam, Siam, Pegu, Bengal, and Malabar. The twig soon becomes encrusted with a reddish substance, which concretes, and consists of the inspissated juice of the plant imbued with coloring matter derived from the insect. The twigs thus encrusted constitute the *stick-lac* of commerce; this, when taken off the twigs, coarsely pounded, and washed with water so as to remove a great portion of the coloring substance, forms the article known as *seed-lac*; and this, when fused, strained, and dropped upon a smooth surface, so as to spread out into thin brittle plates on cooling, constitutes what is termed *shell-lac*. These varieties of lac have been chemically examined by Hatchett, in 1804 (*Phil. Trans.*), by John, in 1810 (*Chem. Untersuchungen*, i. 52), and by Unverdorben, in 1828. (*Poggend. Ann.*, xiv. 116.) The latter chemist distinguishes no less than five distinct resins, together with coloring and fatty matter, and a resinoid, to which John gave the name of *laccine*. Hatchett's results are as follows :

|                       | Stick-lac. |      | Seed-lac. |      | Shell-lac. |
|-----------------------|------------|------|-----------|------|------------|
| Resin .....           | 68·0       | .... | 88·5      | .... | 90·9       |
| Coloring matter ..... | 10·0       | .... | 2·5       | .... | 0·5        |
| Wax .....             | 6·0        | .... | 4·5       | .... | 4·0        |
| Gluten .....          | 5·5        | .... | 2·0       | .... | 2·8        |
| Foreign bodies .....  | 6·5        | .... | ....      | .... | ....       |
| Loss.....             | 4·0        | .... | 2·5       | .... | 1·8        |
|                       | <hr/>      |      | <hr/>     |      | <hr/>      |
|                       | 100·0      |      | 100·0     |      | 100·0      |

John gave the name of *laccic acid* to a crystallizable substance, which he found in stick-lac partly combined with potassa. (THOMSON'S *System*, ii. 177.) In 1794 Dr. Pearson examined a substance called *White Lac*, from Madras, in which he found a peculiar acid, which he also called *laccic acid*. (*Phil. Trans.*)

The *coloring matter* of lac is prepared in India, and is extensively used as a scarlet dye-stuff, for the production of which it is a most efficient substitute for cochineal. Two forms of it are imported, called *lac-lake* and *lac-dye*. These substances contain about 50 *per cent.* of the coloring matter, mixed with more or less of the resin, and with earthy matters, said to consist chiefly of chalk, gypsum, and sand. According to Dr. Ure, (*Dictionary of Arts, &c.*,) the cakes of *lac-dye* imported from India, stamped with peculiar marks to designate their different manufacturers, are now employed exclusively, in England, for dyeing scarlet cloth, and are found to yield an equally brilliant color, and one less easily affected by perspiration than that produced by cochineal. The solvent of the lac-dye is dilute sulphuric or hydrochloric acid, especially the latter, and the proper mordant is nitromuriate of tin and tartar. The details of the process are given by Ure and by Dumas. The general characters of the coloring matter of lac appear closely to resemble those

of cochineal and of kermes, but it has not, I believe, been the subject of any specific examination.

Lac is very important in reference to its *resinous components*, as an ingredient in *varnishes* and *lacquers*, and in *sealing wax*. It is used both in oil and spirit varnishes, but there is much difficulty in getting it to dissolve in alcohol, unless it has been very finely pulverized, and then exposed for many months to the action of air. For colorless varnishes it also requires to be bleached, which may be effected by chlorine. A variety of receipts for these varnishes are given by Dumas. (*Chim. App. aux Arts*, vii. 354.) *Red sealing-wax* is made by carefully fusing together 48 parts of shell-lac, 19 of Venice turpentine, and 1 of Peru balsam, to which 32 parts of very finely levigated cinnabar are afterwards added. In the cheaper kinds of sealing-wax red lead is used instead of cinnabar, and there is a large addition of common resin, which causes it to run into thin drops when fused. *Black sealing-wax* is made of 60 parts of shell lac, 10 of Venice turpentine, and 30 of finely-levigated ivory-black. *Yellow sealing-wax* is colored with chromate of lead; *blue*, with smalt; *green*, with carbonate of copper; and *white*, with white lead.

A *spurious lac* is described by Nees and Marquart. (*Ann. der Pharm.*, xiii. 286.)

#### X. COCHINEAL-RED. CARMINE.

*Cochineal* is the female of a species of *Coccus*, which feeds on the *nopal* (*Opuntia Coccinillifera*); it is imported from Mexico. The principal use of cochineal is as a dye-stuff; but its consumption has lately declined, in consequence of the substitution of lac-dye and of madder. A small quantity is also employed for pharmaceutical purposes. A pound of cochineal is said to contain about 70,000 dried insects. A detailed account of the insect, and of the mode of rearing and preparing them for the market, is given by Bancroft. (*Researches concerning the Philosophy of Permanent Colors*.) See also *Pharmaceutical Journal*, vi. 203.

Cochineal consists of the dried female insects, which are from one to two lines in length, wrinkled, of an irregular figure, convex on one side, and nearly flat on the other. They are inodorous, have a bitterish warm taste, tinge the saliva violet-red, and yield a dark crimson powder. When burned, they evolve an animal odor, and leave a grey ash. In water they swell up so as to show their ringed character, and even their feet, giving the liquid a red color. They are distinguished into the *silver* and *black* varieties. *Silver-grain cochineal* has a purplish-grey color, and the furrows appear as if filled with a whitish powder, which, with the aid of a lens, appears like fine wool. *Black-grain cochineal* is purplish-black, and nearly devoid of the silvery character. A system of adulterating cochineal was practised some years ago in London, which consisted in moistening the article with gum-water, and then agitating it first with finely-powdered sulphate of baryta, and then with ivory-black, to give it the appearance of black cochineal. Powdered talc, and carbonate of lead have been used to give the silvery appearance, but a lens will readily distinguish these powders from the real wool which gives the silvery aspect. (PEREIRA, *Mat. Med.*, p. 1852; URE, *Dictionary of Arts, &c.*)



Cochineal was first chemically examined by John in 1813 (*Chem. Untersuchungen*, iii. 210); in 1818 a paper upon it was published by Pelletier and Caventou, and another by Pelletier, in 1832. (*Ann. Ch. et Ph.*, viii. 250, and Li., 194.) Preisser has also examined its coloring principle, (*Erdmann and Marchand's Journ.*, xxxii. 150,) and more lately an elaborate series of experiments upon it have been communicated to the Chemical Society of London, by Warren de la Rue. (*Mem. Chem. Soc.*, iii. 1847.)

According to Preisser, a colorless principle, which by oxidizement acquires color, may be extracted from cochineal by digesting it first in ether, to remove fat, (p. 1269,) and then boiling it in water; from this decoction the coloring matter may be abstracted by means of hydrated oxide of lead, and when this compound is decomposed by sulphuretted hydrogen, the filtered liquor yields yellowish acicular crystals, more soluble in water and in alcohol than in ether, and the colorless aqueous solution of which, gradually reddens if exposed to air, and if boiled, deposits a purple-red precipitate. Preisser calls the colorless substance *carmine*, and the colored precipitate *carméine*.

*Carméine* (*Coccinelline*, *Red carmine*) is obtained, according to Pelletier, as follows: the pulverized cochineal is first deprived of fat by ether; it is then boiled in alcohol, sp. gr. 0.820, as long as it yields color; the greater part of the alcohol is then distilled off, and the residue left to spontaneous evaporation in an open vessel, when a crystallized compound of *carméine*, fat, and animal matter remains, which, treated with cold alcohol, leaves a brown extract-like residue. The *carméine* is precipitated from the alcoholic solution, by mixing it with its bulk of ether. It is of a deep purple-red color, permanent in the air, and soluble in water, to which it communicates a very intense purple hue: it also dissolves in alcohol, but difficultly in proportion as the alcohol is pure. It is insoluble in ether, and in fat and volatile oils. Its composition is  $C_{32}H_{26}O_{20}N$ . Chlorine, iodine, and bromine destroy the color of *carméine*; the dilute acids give it a yellow tint, which reverts to purple on saturating the solution by an alkali. Its aqueous solution is not precipitated by the acids; it is rendered scarlet by bitartrate and binoxalate of potassa. The alkalis render it violet; and when its alkaline solution is exposed to air, oxygen is slowly absorbed, and the coloring-matter decomposed. Hydrate of alumina rapidly abstracts coccinelline from its solution, forming a *pink-lake*, which, on boiling, acquires a violet tinge. Alum renders the solution purple, but occasions no precipitate; acetate of lead gives a violet precipitate; chloride of tin a dark red; the salts of iron a brown, and the salts of copper a violet-colored precipitate. The precipitate with the subsalts of mercury is violet, and scarlet with the salts of the red oxide. Nitrate of silver has little action on the solution of *carméine*, and chloride of gold destroys it. Tannine occasions no precipitate. (PELLETIER and CAVENTOU. PREISSER.)

According to Warren de la Rue, the *carméine*, or coccinelline of Pelletier and Caventou, was rendered impure by phosphoric acid, and by the presence of an azotized substance; to the latter he attributes the nitrogen obtained in Pelletier's analysis. He gives the name of *carminic acid* to the pure coloring principle of cochineal (*carméine*), for he finds that it has the properties of a feeble acid, combining with bases, and being

capable of abstracting some of them from their combinations with acetic acid.

*Carminic Acid*,  $C_{28}H_{14}O_{16}$ , is prepared by precipitating an aqueous decoction of cochineal with acetate of lead, and decomposing the washed precipitate by sulphuretted hydrogen; the red filtrate is then again precipitated by the acetate, and decomposed as before. The filtrate resulting from this second operation is now evaporated to dryness over sulphuric acid *in vacuo*, and the residue dissolved in boiling absolute alcohol; the alcoholic solution is digested with a portion of dry *carminate of lead*, to remove phosphoric acid, and then concentrated, and diluted with an equal bulk of ether, which precipitates the azotized impurity in the form of red flocks, carrying down with them some of the coloring matter; the liquor is then filtered, and on evaporation to dryness, yields pure carminic acid.

Carminic acid, as thus prepared, is a purple-brown friable mass, becoming of a brilliant crimson when triturated into fine powder, and transparent when viewed by the microscope; it is soluble in all proportions in water and in alcohol, and only very slightly soluble in ether; but ether does not precipitate it from its alcoholic solution when it is perfectly free from azotized impurities. Its aqueous solution has a feeble acid reaction; its alcoholic solution is precipitated by ammonia and by the alkalis, and their respective *carminates* are formed. It is soluble, without decomposition, in strong sulphuric and hydrochloric acid, but it is decomposed by nitric acid, and by chlorine, iodine, and bromine.

Carminic acid consists of

|               |       |    |      | W. de la Rue. |            |
|---------------|-------|----|------|---------------|------------|
| Carbon        | ..... | 28 | .... | 168           | .... 54·19 |
| Hydrogen      | ....  | 14 | .... | 14            | .... 4·52  |
| Oxygen        | ..... | 16 | .... | 128           | .... 41·29 |
| <hr/>         |       |    |      | <hr/>         |            |
| Carminic acid |       | 1  |      | 310           | 100·00     |

De la Rue analysed the *carminate of copper*, and found it =  $CuO$ ,  $C_{28}H_{14}O_{16}$ . From a careful repetition of Preisser's experiments above quoted, he concludes that the colorless modification of the coloring principle of cochineal, which that chemist thought he had discovered, does not exist.

*Nitrococcusic Acid*.  $C_{16}H_3O_{16}N_3 + 2HO$ . When carminic acid is boiled in nitric acid, sp. gr. 1·4, it produces oxalic acid, together with a new acid, called by De la Rue, *nitrococcusic acid*; to obtain it pure, the oxalic acid is removed by means of nitrate of lead, and the nitrococcusic acid crystallized out of the filtrate; by two or three recrystallizations it is rendered perfectly pure. This acid is *bibasic*, and all its salts are much more soluble in water than the acid itself; it is of a yellow color, and crystallizes in rhombic plates containing 2 atoms of water of crystallization. In properties and appearance it is very analogous to the nitropicric and nitrostyphnic acids, and deflagrates on being heated, as do likewise its salts; the *silver-salt* is highly explosive. It is soluble in water, alcohol, and ether, and the solutions stain the cuticle yellow. The equivalent of the *anhydrous acid*, as it exists in combination with bases, is 269; its composition being



|                              |    |      |     |      |        |
|------------------------------|----|------|-----|------|--------|
| Carbon .....                 | 16 | .... | 96  | .... | 35.69  |
| Hydrogen .....               | 3  | .... | 3   | .... | 1.12   |
| Oxygen .....                 | 16 | .... | 128 | .... | 47.58  |
| Nitrogen .....               | 3  | .... | 42  | .... | 15.61  |
| <hr/>                        |    |      |     |      |        |
| Anhydrous nitrococcusic acid | 1  |      | 269 |      | 100.00 |

The equivalent of the *hydrate of the acid* is 287; its ultimate elements being

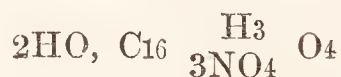
|                                      |    |     |     |     |        |       |  |   |     |     |     |        |
|--------------------------------------|----|-----|-----|-----|--------|-------|--|---|-----|-----|-----|--------|
| Carbon .....                         | 16 | ... | 96  | ... | 33.44  | } = { | Anhydrous<br>nitrococcusic<br>acid ..... | 1 | ... | 269 | ... | 93.73  |
| Hydrogen .....                       | 5  | ... | 5   | ... | 1.74   |       |  |   |     |     |     |        |
| Oxygen .....                         | 18 | ... | 144 | ... | 50.17  |       |  |   |     |     |     |        |
| Nitrogen.....                        | 3  | ... | 42  | ... | 14.65  |       |  |   |     |     |     |        |
| <hr/>                                |    |     |     |     |        |       |  |   |     |     |     |        |
| Hydrated nitro-<br>coccusic acid.... | 1  |     | 287 |     | 100.00 |       |  | 1 |     | 287 |     | 100.00 |
| <hr/>                                |    |     |     |     |        |       |  |   |     |     |     |        |
| <hr/>                                |    |     |     |     |        |       |  | 2 | ... | 18  | ... | 6.27   |
| <hr/>                                |    |     |     |     |        |       |  |   |     |     |     |        |

But the *crystallized acid*, as obtained by the evaporation of its solution in water, is represented by the formula  $C_{16}H_3O_{16}N_3, HO, + 2HO$ .

The following are the formulæ of such of the salts of this acid as have hitherto been analysed :

|                               |                     |  |
|-------------------------------|---------------------|--|
| Nitrococcusate of ammonia.... | 2NH <sub>4</sub> O, | C <sub>16</sub> H <sub>3</sub> O <sub>16</sub> N <sub>3</sub> , + 11O. |
| „ potassa ....                | 2KO,                | C <sub>16</sub> H <sub>3</sub> O <sub>16</sub> N <sub>3</sub> .        |
| „ baryta .....                | 2BaO,               | C <sub>16</sub> H <sub>3</sub> O <sub>16</sub> N <sub>3</sub> , + 2HO. |
| „ silver .....                | 2AgO,               | C <sub>16</sub> H <sub>3</sub> O <sub>16</sub> N <sub>3</sub> .        |

De la Rue observes further, in regard to this acid, that it may likewise be represented by the formula



and that it is therefore isomeric with the *trinitroanisic acid*, of Cahours; the latter, however, is probably a more basic acid, as is the case with *anisic acid*, and its derivative, *nitroanisic acid*.

From the mother-liquor of carminic acid, De la Rue procured a considerable quantity of an *azotized substance*, which could only be dried into a soft uncrystalline solid; but he also obtained from it a *new crystalline body*, bearing a close resemblance in its physical and other characters to the *Tyrosine* of Liebig. 1000 parts of cochineal yielded about 4 parts of this new substance; it crystallizes in fine silky needles, slightly soluble in cold, but much more soluble in hot water, and insoluble in alcohol and in ether. It is soluble both in alkalis and in acids, and appears to be of the class of neutral or indifferent bodies: it is represented by the formula  $C_{18}H_{11}O_6N$ .

The pigment termed *Carmin* is generally made by boiling cochineal with carbonate of potassa or of soda, and precipitating the clear liquor by means of a weak acid, or of an acid salt; a mixture of alum and cream of tartar is frequently used for this purpose, and in some cases, binoxalate of potassa; the precipitation is sometimes accelerated by the use of gelatine or of white of egg. Among the numerous processes for the manufacture of carmine, (see DUMAS, viii. 79, and URE'S *Dictionary*, Art. *Carmin*) the following, called "the Process of Madame Cenette of

Amsterdam," may be taken as a specimen; it is said to afford an article of extraordinary lustre. "Into six pails-full of boiling hot river water, throw 2 pounds of the finest cochineal, in powder; continue the ebullition for 2 hours, and then add 3 ounces of refined salt-petre, and after a few minutes, 4 ounces of salt of sorrel (binoxolate of potassa.) In 10 minutes more, take the copper from the fire, and let it settle for 4 hours; then draw off the liquor with a siphon into flat plates, and leave it there for 3 weeks. There is formed upon the surface a pretty thick mouldiness, which is to be removed dexterously in one pellicle by a slip of whalebone. Should the film tear, and fragments of it fall down, they must be removed with the utmost care. Then decant the supernatant water by means of a siphon, the end of which may touch the bottom of the dish, because the layer of carmine is very firm. Whatever water remains must be sucked away by a pipette. The carmine is then cautiously dried in the shade." The principal consumers of carmine are artists in oil and water colors, and artificial-flower makers; an ammoniacal solution of carmine forms a beautiful transparent color, and constitutes a superior description of *red ink*. Carmine may be purchased at different prices dependent upon its purity; it often includes a considerable quantity of alumina, and not frequently, of vermilion. It has been asserted that the superiority of French over English carmine depends upon the influence of light upon its formation and precipitation, and that the clear sky of parts of France is more favorable for the process, than the comparatively hazy atmosphere of England. (See an anecdote by Sir H. Davy, in his "*Salmonia*." *Collected works*, ix. 61.)

## XI. YELLOW COLORING-MATTERS.

The vegetables which afford the different shades of *yellow*, used as pigments, and in the arts of dyeing and calico-printing, are very numerous, but definite crystallizable principles have been but in a few instances obtained from them.

In the following paragraphs the leading characters of such as have been studied with any degree of attention will be enumerated.

1. ANNOTTA. This substance, the *Roucou* of the French, and *Orleans* of the Germans, is derived from the pulp of the seeds of the *Bixa Orellana*, a shrub native in South America, but cultivated in Guiana and St. Domingo, and also in the East Indies; it appears to have been used by the natives as a dye-stuff, and to have been made known in Europe soon after the conquest of Mexico by the Spaniards. It is chiefly imported from America, in cakes of two or three pounds weight, wrapped in large leaves and packed in casks. It is said to be obtained from the rasped or ground seeds, mixed with water, and suffered to ferment, or rather to putrefy; the pulp is then strained through sieves, and boiled down the consistence of a paste. Leblond, who imported the seeds into France, (URE's *Dictionary*, Art. *Annotta*), found this tedious process unnecessary, inasmuch as the coloring matter lies wholly on the surface of the seeds, and may be speedily removed by the solvent power of water, from which solution the color is precipitated by a weak acid, and may be dried in the usual way.



Annotta appears in the form of a pasty substance, of a deep orange-red color, nearly tasteless, but of a very disagreeable odor, derived from its being moistened from time to time in the warehouses by the affusion of urine. When heated it softens, burning with much flame and smoke, and leaving a bulky brilliant coal. It is little soluble in water, but alcohol and ether act upon it more readily, forming solutions which, when evaporated, leave the coloring matter in the form of powder. It is abundantly soluble in the alkalis and their carbonates, forming dark-red liquors, in which the acids occasion an orange-red precipitate. Neither hydrochloric nor acetic acid have much action on annotta, but with sulphuric acid it forms a blue solution, which gradually passes into green and violet. When heated with nitric acid there is violent action, and even inflammation. It dissolves in oil of turpentine, and in the fixed oils. (BOUSSINGAULT, *Ann. Ch. et Ph.*, xxviii. 440.)

According to Chevreul (*Chimie app. à la Teinture*), annotta contains a yellow and a red coloring matter; the former, soluble in water and in alcohol, and slightly soluble in ether, and giving a yellow dye to silk and wool mordanted with alumina; the latter, little soluble in water, but soluble in alcohol and ether, and in the alkalis, and rendered blue by sulphuric acid. Annotta is sometimes adulterated with brick-dust, colcothar, and other substances; these are detected on burning it to an ash. (GIRARDIN, *Journ. de Pharm.*, xxii. 101.) According to Preisser, two substances may be obtained from annotta, which he terms *orelline* and *orelléine*. (Erdmann and Marchand's *Journ.*, xxxii. 158.)

*Orelline* is obtained by digesting annotta in a weak solution of carbonate of soda, and adding hydrated oxide of lead to the dark-brown liquor: the precipitate is then decomposed by sulphuretted hydrogen, and on rapidly evaporating the filtered liquor, the *orelline* is deposited as it cools, in white or very pale yellow acicular crystals, of a disagreeable bitter taste, soluble in water, alcohol, and ether. It gradually becomes yellow by exposure to air and oxidizing agents.

*Orelléine* is, according to Preisser, derived from *orelline*, under the joint influence of air and ammonia; it does not crystallize, but assumes the form of a brown-red powder, forming an indigo-blue solution with sulphuric acid, and combining with the alkalis and oxide of lead. It has the general properties of the original annotta.

Annotta is chiefly used as a dye for silk, giving various shades of orange. The color which it imparts is less affected by soap, acids, and chlorine, than most other similar dyeing materials, but it does not well resist the joint agency of light and air. In Gloucestershire and Cheshire it is used to color cheese, and sometimes butter.

2. QUERCITRON. The inner bark of the *Quercus nigra*, or *tinctoria*, is known under this name; it is a native of North America, but has been introduced into France and Bavaria. Its dyeing powers were first made known by Bancroft, in 1784, and an Act of Parliament was passed in 1786, vesting in him the exclusive use and application of it as a dye-stuff, for a certain term of years. It is prepared for use, by taking off the epidermis and pounding the inner part in a mill. (THOMSON, *Veg. Chem.*, 412.)

The general characters of a decoction made by boiling 1 part of quer-

citron bark with 10 of water, for a quarter of an hour, and straining it, are as follow: it is of a yellowish-brown color, having the odor of oak-bark, a bitterish astringent taste, and slightly reddening litmus. It forms a reddish flocculent precipitate with solution of isinglass, and holds chlorides and sulphate of lime in solution. Alkalis deepen its color, and the alkaline earths occasion dirty yellow precipitates. With acid protochloride of tin it gives a reddish precipitate. Alum produces a slight deposit after some hours. With acetate of lead the precipitate is reddish-yellow, and greenish-yellow with acetate of copper. With persulphate of iron it becomes green, and deposits a green flocculent precipitate. Sulphuric and nitric acids throw down yellowish and reddish flocks.

*Quercitrine*. When a strong aqueous decoction of quercitron bark is first precipitated by gelatine to separate tannine, and then shaken with a very small quantity of hydrated oxide of lead, a dirty brown precipitate falls, from which a bright yellow solution may be poured or filtered off. To this, a larger quantity of hydrated oxide of lead is then added, and the resulting precipitate decomposed by sulphuretted hydrogen; on filtering from the sulphuret of lead, a colorless liquor is obtained, which, on evaporation *in vacuo*, yields colorless acicular crystals of *quercitrine*. (PREISSER, *Erdmann and Marchand's Journ.*, xxxii. 111.) It has a sweetish bitter taste, and is soluble in water, alcohol, and ether. On exposing its aqueous solution to air, it becomes deep-yellow and deposits a yellow precipitate: if this solution be boiled in a shallow basin, it becomes turbid, and deposits a quantity of yellow acicular crystals of *quercitréine*.

Quercitrine forms yellow solutions with the dilute mineral acids. With the alkalis its solution, if exposed to air, is dark brownish-yellow. With acetate of lead the precipitate is white, and may be dried without change of color, provided air be excluded. According to Preisser, the formula of quercitrine is  $C_{32}H_{15}O_{14}$ ; and that of its lead-compound,  $PbO, + 2[C_{32}H_{15}O_{14}]$ .

*Quercitréine* was first obtained by Chevreul from a decoction of 1 part of the bark in 5 of water, which, after some days, deposited crystalline quercitréine. Bolley obtains it from an alcoholic tincture of quercitron bark which has been deprived of tannine by a solution of gelatine. (*Ann. der Pharm.*, xxxvii. 166.) Quercitréine is either crystalline or pulverulent, yellow, inodorous, and slightly bitter. It is much less soluble in water than quercitrine; it dissolves in from 4 to 5 parts of alcohol; its solution is slightly acid, and after long exposure to air becomes reddish-brown: alkalis give it a greenish-yellow hue; it is entirely deprived of color by hydrated oxide of lead, which produces with it a golden-yellow precipitate. It gives a brown precipitate with nitrate of silver, which soon decomposes, and the metal is reduced. With acetate of copper and chloride of tin, it gives a yellow, and, with persulphate of iron, an olive-green precipitate. A solution of alum brightens the color of a solution of quercitréine, and on adding an alkali, the precipitate is of a fine yellow. Quercitréine has been analysed by Bolley, who assigns to it the formula  $C_{32}H_{17}O_{20}$ , when dried at  $212^{\circ}$ . From its combination with oxide of lead, Preisser deduces the formula  $C_{32}H_{15}O_{18}$ , for *anhydrous quercitréine*, and represents it in its *crystalline* form as  $C_{32}H_{15}O_{18} + 2HO$ . A decoction of quercitron bark



deprived, by a little glue, of its tannine, produces a fine yellow upon fabrics mordanted with alumina; and various shades of olive, with iron mordants. It is an article of extensive utility in calico-printing.

3. FUSTIC. This dye-stuff, the *bois-jaune* of the French, is the wood of the *Morus tinctoria*, a large tree which grows in Brazil, Jamaica, and most of the West Indian Islands. When a concentrated decoction of fustic cools, it deposits a yellow crystalline matter, which Chevreul examined in 1818, and gave it the name of *morine*. (*Ann. Ch. et Ph.*, ix. 330. *Chimie app. à la Teinture*, ii. 152.) One part of fustic boiled in 10 of water for a quarter of an hour, gives a yellow decoction which gradually deposits *morine*. The decoction is inodorous, slightly astringent and bitter, and precipitates gelatine. It is rendered orange-colored, or greenish-brown, by alkalis. With protochloride of tin, and with alum, it gives yellow precipitates; orange-colored with acetate of lead, yellow-brown with acetate of copper, and dark olive with persulphate of iron. With sulphuric acid it gives an orange-colored precipitate, soluble in excess of the acid; it is reddened by nitric acid, and rendered paler by oxalic acid, and by acetic acid. Chlorine slightly precipitates it, at first deepening, and then destroying its color. According to Preisser, the yellow coloring matter of fustic is oxidized *morine*, or *moréine*. The yellow of fustic is said to unite well with indigo to produce various greens.

4. WELD. This, which is the *gaude* or *vaude* of the French, and *vaugelj* of the Germans, is the dried leaves and stem of the *Reseda luteola*, a plant indigenous in Britain and other parts of Europe. The whole herb is gathered when in seed, at which period its dyeing power is greatest. There are two kinds of weld, the cultivated and the wild; the former is richest in coloring matter. The decoction of this plant has a slight acid reaction and a greenish-yellow color, which is deepened by alkalis, and rendered paler by dilute acids. With alum, acetate of lead, or protochloride of tin, it produces a yellow lake; sulphate of iron blackens it, and with sulphate of copper it gives a brown precipitate. By treating a decoction of weld with hydrated oxide of lead, decomposing the resulting compound by sulphuretted hydrogen, and evaporating the filtered liquor, Preisser obtained a white substance to which he has applied the name of *luteoline*. It is volatile, subliming, when cautiously heated, in yellow and white needles. The alkalis render its solution deep yellow, by converting it into *luteoléine*.

*Luteoléine* was first obtained by Chevreul; it forms a yellow crystalline sublimate, sparingly soluble in water, but more abundantly in alcohol and ether. The yellow which weld communicates to goods mordanted with alum, is very permanent, but, according to Bancroft, when it is employed in calico-printing, a heat nearly as high as that of boiling water is necessary to fix its color, and the parts required to be kept white, are at that temperature so deeply stained by it, as to render it difficult to bleach them. Almost all these simple vegetable yellows, however, have been to a great extent superseded, as far as calico-printing is concerned, by the use of chromate of lead.

*Serratula tinctoria*, or *sawwort*, and *Genista tinctoria*, or *dyers'*

*broom*, contain coloring principles closely allied to, if not identical with, that of weld.

5. PERSIAN BERRIES. Under this name the berries of the *Rhamnus tinctoria* are known amongst painters and calico-printers. In France they are called *grains d'Avignon*. They were first chemically examined by Chevreul, and afterwards by Henry (*Erdmann and Marchand's Journ.*, xxvi. 226); by Kane (*Ann. Ch. et Ph.*, 3ème Sér., viii. 380); and by Preisser. These berries vary in size; the largest, which are olive-green, and appear to be the mature berry, are most esteemed; the smaller ones are brown and wrinkled, and have probably been suffered to remain longer upon the branches. The coloring matter, according to Kane, is distinct in these two varieties. Preisser asserts that in this, as in other cases, the coloring principle may be brought to a colorless state, by reducing agents; and, when in this form, he has termed it *rhamnine*.

*Rhamnine* is obtained from an ethereal tincture of the berries, which after having been reduced by distillation to about one-third its original bulk, is mixed with water, and a small quantity of hydrated oxide of lead; it is then filtered, and the entire coloring matter abstracted from the clear yellow liquor, by the further addition of the hydrated oxide; this lead-compound is then decomposed by sulphuretted hydrogen, the clear filtrate evaporated to dryness, and the residue washed with ether. *Rhamnine* is an almost colorless crystalline powder, of a bitter taste, and soluble in water, alcohol, and ether. These solutions soon acquire a yellow color by exposure, the *rhamnine* passing into *rhamnénine*. Nitric and chromic acids, bichromate of potassa, and other oxidizing agents, immediately produce the same change, and, under the influence of alkalis, the liquors acquire a dark-brown color. (PREISSER.)

*Chrysorhamnine*. *Rhamnénine*. This substance was obtained from the green berries by means of ether; it has a golden-yellow color, and is crystallizable; it is almost insoluble in cold water, but soluble in alcohol and ether. After having been dried at  $212^{\circ}$ , it consists, according to Kane, of  $C_{23}H_{11}O_{11}$ . When its alcoholic solution is decomposed by acetate of lead, a fine yellow precipitate falls, which, after having been dried at  $212^{\circ}$ , is  $= 2PbO, + C_{23}H_{11}O_{11}$ .

When *chrysorhamnine* is boiled in water, and in the contact of air, it passes into *xanthorhamnine*,  $= C_{23}H_{12}O_{14}$ .

|                                |                      |
|--------------------------------|----------------------|
| 1 atom of chrysorhamnine ..... | $C_{23}H_{11}O_{11}$ |
| 1 „ water .....                | $H\ O$               |
| 2 „ oxygen .....               | $O\ 2$               |
| <hr/>                          |                      |
| = 1 „ xanthorhamnine .....     | $C_{23}H_{12}O_{14}$ |

*Xanthorhamnine* is contained in the brown shrivelled Persian berries, from which it may be obtained by hot water; it is insoluble in ether, but readily soluble in water and in alcohol, and remains on evaporation, in the form of an extract. Kane found its compound with oxide of lead to be  $2PbO, C_{23}H_{12}O_{14}, + 3HO$ .

6. TURMERIC. This is the root of the *Curcuma longa*, a plant which is a native of the East Indies, and much cultivated about Calcutta, and in



all parts of Bengal; also in China and Cochin-China. One acre is said to yield about 2000 pounds of the fresh root. The root, or more properly the *tubers*, called *turmeric*, are sometimes distinguished into *round* and *long*. The first is about 2 inches long and an inch in diameter, pointed at one end, and wrinkled. The second is cylindrical, about the thickness of the little finger, 2 or 3 inches long, somewhat contorted, and tuberculated. Both kinds are grayish-yellow externally, internally more or less orange-yellow, passing into brown. The fractured surface has a waxy appearance. The odor is aromatic and peculiar; the taste aromatic. When chewed it tinges the saliva yellow. Its powder is orange-yellow. The tubers are frequently worm-eaten. It is employed as a condiment, coloring-matter, and test, and is a constituent of *currey powder*, and *currey paste*. (PEREIRA, *Mat. Med.*, 1021.)

*Curcumine*, or the coloring-matter of turmeric, has been examined by Pelletier and Vogel (*Journ. de Pharm.*, v. 289); by Batka (*Ibid.*, xvi. 226); and by Vogel Jun. (*Ann. Ch. et Ph.*, 3ème Sér., viii. 276.) It is obtained by treating the watery extract of turmeric by boiling alcohol of sp.gr. 0.80, and evaporating the filtered tincture. The residue is digested in hot ether, which dissolves the curcumine, together with traces of volatile oil and chloride of calcium; this solution is evaporated, the residuum dissolved in alcohol, and precipitated by an alcoholic solution of acetate of lead; the precipitate is diffused through water, decomposed by sulphuretted hydrogen, and the resulting precipitate dried and treated with ether, which dissolves the pure curcumine, and leaves sulphuret of lead.

Curcumine is deposited, on the evaporation of the ether, in the form of an inodorous, transparent, reddish substance, not crystalline, and acquiring a fine yellow color when rubbed to powder. It fuses at  $105^{\circ}$ , and is scarcely soluble, even in hot water, but readily soluble in alcohol and ether, and in fat and volatile oils. It therefore approaches in its characters to those of the resins. Vogel found, as the mean of four analyses, that, prepared as above described, it consisted of 69.5 *per cent.* of carbon, 7.4 of hydrogen, and 23.1 of oxygen.

With sulphuric, hydrochloric, and phosphoric acid, it produces red solutions; and on the addition of water, a pale green flocculent precipitate falls. Nitric acid decomposes it; acetic acid dissolves it without change. When boracic acid is added to an alcoholic solution of curcumine, no change of color ensues, but on evaporation, a crimson-colored compound remains. Curcumine forms reddish-brown solutions with the alkalis, and the salts of lead and of peroxide of uranium produce the same change of tint. When turmeric paper is acted on by hydrochloric acid gas, it is reddened, and boracic acid and some of the borates produce the same effect. *Turmeric paper* for the use of the laboratory is best prepared with a strong tincture of turmeric in proof-spirit, the same precautions in regard to paper, &c., being observed, as mentioned in respect to the preparation of litmus paper.

7. SUMACH. *Young fustic*. This substance consists of the dried and bruised branches of the *Rhus coriaria*, and *Rhus cotinus*, natives of Italy and of the South of France, where it is cultivated for the double purpose of a dyeing and tanning material. In the South of France the

leaves of the *Rhus myrtifolia* are also used for dyeing, under the name of *redoul* or *rodou*. Sumach has not been minutely examined, but it yields, according to Chevreul, a yellow crystallizable coloring-matter, which Preisser has separated as follows: the tannine is first precipitated from the decoction, by means of gelatine, and on filtering, a greenish-yellow liquor is obtained, which is to be evaporated nearly to dryness, and the residue treated with ether: this solution is then evaporated in a retort, and water added to the residue, together with hydrated oxide of lead, which forms a yellow compound, to be decomposed by sulphuretted hydrogen; the liquor filtered from the sulphuret of lead yields small yellowish crystals, which may be purified by washing with ether: these constitute *fustine*.

*Fustine* is slightly bitter, and is soluble in water, alcohol, and ether, and these solutions acquire color by exposure to air. With sulphuric and nitric acid it forms yellow solutions. Its precipitate by acetate of lead is at first white, but it gradually grows yellow: with persulphate of iron the precipitate is dark olive. Potassa, soda, and ammonia, immediately redden it. *Fustine* has a great tendency to absorb oxygen, and on the whole, it appears closely to resemble rhamnine. (DUMAS. *Chim. app. aux Arts*, viii. 112.)

8. CHRYSOPHANE. Under this name Löwig has described the coloring-matter of *rhubarb*, and of *Lichen parietarius*: the former has also been termed *Rhéine* or *Rhabarbarine*, and the latter *Parietine*. Many analyses of the root of *rhubarb* (*Rheum palmatum*, &c.,) have been published, (see PEREIRA'S *Mat. Med.*, p. 1182,) chiefly with a view of determining the source of its medicinal activity, which has been successively ascribed to a bitter principle, to an organic basis, to an acid, to a gum, to a resin, and to a coloring-matter. The latest researches of Schlossberger and Döpping (*Ann. der Pharm.*, L. 196,) have shown that the coloring-principle of *rhubarb*, to which the terms *rhéine* and *rhabarbarine* have especially been applied, is identical with the substance termed *parietine*, the coloring-matter of the *Lichen parietinus*, as obtained by Rochleder and Heldt. (*Ibid.*, XLVIII. 12.) The former chemists have also discovered three resinoid substances in *rhubarb*, namely *Aporetine*, *Phæoretine*, and *Erythroretine*, together with extractive matter, and they ascribe the medical virtues of the root, not to any one principle, but to a mixture of several, amongst which are tannine and gallic acid.

*Chrysophane* was obtained from *rhubarb*-root as follows: the alcoholic extract of *rhubarb* was treated with water, then dried, and dissolved in as little alcohol as possible. The alcoholic solution was then mixed with ether, by which *aporetine* and *phæoretine* were thrown down; the ether was distilled from the remaining clear solution, and the residue which it left, dissolved in alcohol, again precipitated by ether, and the precipitate having been separated, this ethereal solution was again distilled to dryness. The dry residue was finally digested in ether, which took up *chrysophane* and *erythroretine*, and the solution was left to spontaneous evaporation in a covered basin, when the *chrysophane* crystallized, leaving the *erythroretine* dissolved in the remaining ether. The *chrysophane* was purified by re-solution in ether, and recrystallization. (SCHLOSSBERGER and DÖPPING.) Brandes and Geiger



have each proposed modifications of this process: the method of Geiger is even more troublesome and tedious than the above. Brandes merely directs the concentrated ethereal tincture of rhubarb to be so far distilled as to separate a great part of the ether, and states that small brown granular crystals of chrysophane are gradually deposited from the residue, which may be purified by repeated solution in, and crystallization from alcohol. (*Ann. der Pharm.* ix. 85. See also LÖWIG, *Chem. d. Org. verbind.*, i. 880, for the details of these and other processes.)

From *Lichen parietinus* chrysophane is obtained by digesting it for some time in an alcoholic solution of potassa, straining off the red tincture, and neutralising it with acetic acid, when a bulky precipitate of chrysophane falls, which, after having been well washed with water, is to be again dissolved in the alkaline alcoholic solution, and again precipitated by acetic acid. This precipitate, after having been washed, and dried at  $212^{\circ}$ , is to be dissolved in a small quantity of boiling alcohol, and the hot filtered solution allowed to cool very slowly, when crystals of chrysophane are formed. Chrysophane may also be extracted from the lichen by means of ether. (ROCHLEDER and HELDT.)

Chrysophane, as obtained from the lichen, forms golden-yellow groups of stellated crystals, which, after having been dried at  $212^{\circ}$ , assume somewhat of the appearance of iodide of lead. Obtained from rhubarb it is generally a bright yellow granular deposit. It is difficultly soluble in alcohol and ether, almost insoluble in cold, and very sparingly soluble in boiling water, and little soluble in the dilute mineral acids, and in acetic acid. When carefully heated it is partly decomposed, but the greater portion sublimes, and condenses in the form of gold-colored needles. It dissolves without decomposition in cold concentrated nitric acid, forming a deep-yellow solution, and is thrown down unaltered on the addition of water; but if the solution be heated, a red substance is formed, which gives a fine purple solution with ammonia, not altered by the addition of acetic acid. Boiled in solution of potassa, it evolves ammonia, and is changed into an insoluble substance of a violet color. With concentrated sulphuric acid, chrysophane produces a deep red solution, and is precipitated unchanged, in the form of yellow flocks, on dilution.

Chrysophane is abundantly soluble in alkaline solutions, forming purple liquors. The solution in potassa may be evaporated to dryness without any evolution of ammonia, but when it has attained a certain degree of concentration, a purple compound of chrysophane and potassa is thrown down, forming a flocculent precipitate, soluble in water, and in alcohol. Chrysophane boiled in baryta water produces a red insoluble compound, which, exposed to air, acquires a yellow color, and is decomposed by carbonic acid. When an alcoholic solution of chrysophane is mixed with subacetate of lead, a whitish precipitate falls, which at first dissolves when boiled in water, but immediately afterwards produces an insoluble compound of a splendid carmine color, which shrinks when dried, and yields a cinnabar-red powder. In its moist state it is decomposed by the carbonic acid of the air. With oxide of copper chrysophane produces a blue compound.

The formula of chrysophane deduced from its analysis by the above-quoted chemists, is  $C_{10}H_4O_3$ , but Thomson, as quoted by Löwig,

represents *parietine* as  $C_{40}H_{16}O_{14}$ , and as passing, when in alcoholic solution, into  $C_{40}H_{16}O_{16}$ ; he therefore gives the following series:

|                          |                      |
|--------------------------|----------------------|
| Chrysophane .....        | $C_{40}H_{16}O_{12}$ |
| Parietine .....          | $C_{40}H_{16}O_{14}$ |
| Oxidized parietine ..... | $C_{40}H_{16}O_{16}$ |

But, as regards the equivalent of chrysophane, experiments are still wanting for its accurate determination, and it would appear that as yet no sufficiently definite compound has been analyzed from which its atomic weight might be deduced. The equivalent assumed by Liebig is 88, which sufficiently agrees with the *per centage* results; it represents it (dried at  $212^{\circ}$ ) as

|                            |    |      |    |      |        | Rochleder<br>and Heldt. | Schlossberger<br>and Döpping. |
|----------------------------|----|------|----|------|--------|-------------------------|-------------------------------|
| Carbon .....               | 10 | .... | 60 | .... | 68.18  | .... 68.45              | .... 68.69                    |
| Hydrogen .....             | 4  | .... | 4  | .... | 4.55   | .... 4.56               | .... 4.24                     |
| Oxygen .....               | 3  | .... | 24 | .... | 27.27  | .... 26.99              | .... 27.07                    |
| <hr/>                      |    |      |    |      |        |                         |                               |
| Anhydrous chrysophane .... | 1  |      | 88 |      | 100.00 | 100.00                  | 100.00                        |

9. BERBERINE. This is a coloring principle derived from the root of the barberry tree (*Berberis vulgaris*), in which it was discovered by Buchner and Herberger, (*Buchner's Repert.*, xxvi., *Journ. de Pharm.*, xvii. 40; and xxi. 309 and 408.) To obtain it, the root is exhausted by boiling water, and the decoctions concentrated to the consistence of extract, which is repeatedly digested in alcohol of sp. gr. 0.844 as long as that liquid acquires a bitter taste. These tinctures are then filtered, and a considerable portion of the alcohol having been distilled off, the residue is left to crystallize in an open vessel in a cool place. The resulting crop of crystals having been freed from mother-liquor, and washed with a little cold water, is redissolved in a small quantity of boiling water, and recrystallized. Lastly, it is dissolved in and crystallized from boiling alcohol.

Berberine thus obtained is in the form of delicate silky crystals of a bright-yellow color, inodorous, intensely bitter, and requiring as much as 500 parts of water at  $50^{\circ}$  for solution, but soluble in all proportions in boiling water; it is soluble in 250 parts of cold, but more soluble in hot alcohol; it is neither acid nor alkaline. Some of the fat and volatile oils dissolve it when aided by heat, but it is insoluble in ether and in sulphuret of carbon. It acquires a reddish tint when heated to  $212^{\circ}$ , but regains its yellow color on cooling; at  $265^{\circ}$  it fuses, and at a higher temperature exhales the odor of burned horn, and leaves a difficultly-combustible carbon. Submitted to dry distillation, it produces a yellow ammoniacal liquor. It dissolves in cold nitric acid with the production of abundant fumes, forming a deep-red liquor, which on being heated, loses color, and contains oxalic acid. Acted on by dry chlorine, it acquires a blood-red color and increased solubility in water; but when chlorine is passed through the aqueous solution of berberine, a brown substance is thrown down, soluble in alkaline solutions, from which it is again precipitated by an acid: this precipitate is only partially soluble in alcohol. Bromine and iodine appear to be without action on berberine. Sulphuric acid dissolves it, and on dilution, a brown substance is thrown down, insoluble in water and in alcohol, but soluble in alkalis. Hydrochloric



and phosphoric acid are without action upon berberine, but it dissolves in acetic, tartaric, citric, and oxalic acid, and on evaporating these solutions, the berberine separates unchanged. Infusion of galls precipitates berberine of a brown color.

Berberine acts as an acid in respect to bases, forming compounds of a brown hue, and from which the berberine is separated by the acids. The combinations with ammonia, potassa, and soda may be obtained in small brown crystals. Lime-water occasions no precipitate in a solution of berberine, but baryta-water throws down a yellow flocculent precipitate. When berberine, dissolved in warm water, is added to solutions of the metallic salts, combinations of the metallic oxide with berberine are precipitated; these precipitates are *yellow* with the salts of manganese, cobalt, antimony, tin, mercury, and silver; *green*, with the salts of copper and nickel; *orange-colored*, with the perchlorides of iron, gold, and platinum, and with nitrate of bismuth: the salts of lead, zinc, and protoxide of iron give no precipitate. The compound of berberine with oxide of silver, after having been dried at  $212^{\circ}$ , contains 25.98 *per cent.* of oxide.

The action of berberine upon several of the haloid salts is very peculiar; thus a warm aqueous solution of berberine added to a solution of bromide or of iodide of potassium, produces a bulky pale-yellow precipitate; with cyanide of potassium the precipitate is orange-colored, and soluble in water, and green with ferrocyanide of potassium. Sulphocyanide of potassium produces a pale yellow, and sulphuret of potassium a brown precipitate; no precipitation ensues with chloride of potassium.

Linen, cotton, wool, and silk, may be dyed with berberine, without the intervention of bases, but the color is rendered brighter and more permanent when a tin mordant is used.

The formula assigned to berberine (dried at  $212^{\circ}$ ) is  $C_{33}H_{18}O_{12}N$ ; its composition being

|                 |    |      |     |      |        | Buchner.   |
|-----------------|----|------|-----|------|--------|------------|
| Carbon .....    | 33 | .... | 198 | .... | 60.74  | .... 61.23 |
| Hydrogen .....  | 18 | .... | 18  | .... | 5.52   | .... 5.49  |
| Oxygen .....    | 12 | .... | 96  | .... | 29.45  | .... 29.25 |
| Nitrogen .....  | 1  | .... | 14  | .... | 4.29   | .... 4.03  |
| <hr/>           |    |      |     |      |        |            |
| Berberine ..... | 1  |      | 326 |      | 100.00 | 100.00     |

10. PHLOBAPHENE (*φλοιὸς bark, βαφή a dye-stuff.*) This term has been applied by Stähelin and Hofstetter (*Ann. der Pharm.*, Li. 63) to a yellow-brown coloring substance extracted from the bark of several trees, especially of the *Scotch fir*, *Plane*, and *Birch*. (*Pinus silvestris*, *Platanus acerifolius*, and *Betula alba*.) It may be obtained from fir-bark by digesting it first in ether, and then in alcohol; the alcoholic tincture is evaporated, and the brown residue, after having been exhausted by ether, is dissolved in a small quantity of boiling alcohol, and the solution gradually poured into boiling water, during constant stirring; the reddish-brown precipitate which falls is collected as quickly as possible, washed with hot water, and dried out of contact of air. *Hydrated phlobaphene* is obtained when the bark, having been exhausted by ether, is digested in a weak solution of caustic alkali; from this solution it is thrown down by dilute sulphuric acid.

*Anhydrous phlobaphene* is of a reddish-brown color, insoluble in water, alcohol, and dilute acids, but readily soluble in alkalis. It is inodorous and tasteless, and fuses when heated, and then burns with a sooty flame, leaving a coal of difficult incineration. It is unaltered in the air. The phlobaphene recently thrown down from its alkaline solution differs from the anhydrous, in being soluble in water and in alcohol. The salts of baryta and of lime produce brown precipitates in the ammoniacal solution of phlobaphene. The precipitate with acetate of lead varies in composition, being either  $= 4\text{PbO} + 3[\text{C}_{20}\text{H}_8\text{O}_8 + \text{HO}]$ , or  $4\text{PbO} + \text{C}_{20}\text{H}_8\text{O}_8 + 3\text{HO}$ . The formula assigned by the above-quoted chemists, for *anhydrous phlobaphene*, being  $\text{C}_{20}\text{H}_8\text{O}_8$ . (Löwig, i. 897.)

11. USNINE. USNIC ACID. Knop has given these names to a substance extracted from different *lichens* of the genus *Usnea*, such as *florida*, *hirta*, *plicata*, *barbata*, &c.; it has also been found in *lichens* belonging to the genus *Cladonia*, *Parmelia*, and *Lecanora*, and some others. (*Ann. der Pharm.*, xlix. 103.) It appears in some respects to resemble the principle above described under the name of *Chrysophane*, derived from *Lichen parietinus*, (p. 1521.) Usnine is obtained by macerating the lichen for some days in ether; the greater part of the ether is then distilled off, and on adding alcohol to the residue the usnine falls as a crystalline precipitate: it is purified by washing it with hot alcohol.

*Usnine* crystallizes from its alcoholic solution in brittle prismatic crystals of a sulphur-yellow color, and very electrical when reduced to powder. It is insoluble in water, and very difficultly soluble in alcohol and in cold ether, but much more abundantly so in hot ether. It also dissolves in hot oil of turpentine and fat-oils, which on cooling deposit it again in crystals. At about  $390^\circ$  it fuses like a resin, and concretes into a crystalline mass on cooling; at a somewhat higher temperature it rises in the form of an excessively acrid vapor, which condenses in acicular crystals, but a portion of it is always at the same time decomposed.

Usnine is not affected by chlorine, nor by dilute acids. Concentrated nitric acid converts it into a brown resin of a peculiar odor. Sulphuric acid dissolves it, but it is again thrown down by the addition of water. Hydrochloric acid has no effect upon it. It dissolves in caustic alkaline solutions, and exposed to air, the liquor acquires a red color; on adding to it acetic acid, a yellow precipitate falls, soluble in alcohol, and remaining in the form of a yellow powder when the alcohol is evaporated. When this yellow substance is fused, it reddens, and forms a bright-red solution in sulphuric acid; but when this is diluted, the precipitate is again yellow. When the alkaline solution of usnine is long exposed to air, or when it is boiled, the addition of acetic acid throws down a black tar-like matter, and the remaining liquor is brown. These products of the oxidizement of usnine are not altered by sulphuretted hydrogen.

Usnine acts as a weak acid, producing crystallizable compounds with the alkalis, which are difficultly soluble in water, but soluble in alcohol. These combinations are only produced by pure usnine, free from the products of its oxidizement. Several of these salts have been examined



by Knop, and by Rochleder and Heldt, (*Ann. der Pharm.*, XLviii. 8,) whence the formula  $C_{38}H_{17}O_{14}$  has been obtained for usnine. The following are the results of its analysis, after having been dried at  $212^{\circ}$ :—

|                |    |      |     |      |        | Rochleder<br>and Heldt. | Knop.      |
|----------------|----|------|-----|------|--------|-------------------------|------------|
| Carbon .....   | 38 | .... | 228 | .... | 63.84  | .... 63.76              | .... 63.76 |
| Hydrogen ..... | 17 | .... | 17  | .... | 4.77   | .... 4.88               | .... 4.95  |
| Oxygen .....   | 14 | .... | 112 | .... | 31.39  | .... 31.36              | .... 31.29 |
| <hr/>          |    |      |     |      |        |                         |            |
| Usnine .....   | 1  |      | 357 |      | 100.00 | 100.00                  | 100.00     |

12. EUXANTHINE. *Euxanthic Acid*. (ERDMANN.) *Purreic Acid*. (STENHOUSE.) A substance under the name of *Purree*, or *Indian yellow*, is imported from India and China; its origin has not been well ascertained, but it is supposed by Stenhouse to be the juice of some unknown plant, mixed with magnesia. It has an odor somewhat resembling that of castor, and was therefore suspected to be of animal origin, and derived, perhaps, from the gall of the elephant or camel. The crystallizable principle which it contains, and which may be conveniently termed *euxanthine*, (LÖWIG, i. 888,) may be separated by boiling the crude purree in water, and treating the residue, which is of a fine yellow color (*euxanthate of magnesia*) with hot dilute hydrochloric acid. The euxanthine crystallizes as the liquor cools, and may be purified by dissolving the washed crystals in alcohol, and recrystallizing. It may also be obtained pure, by decomposing a hot solution of crystallized *euxanthate of ammonia* by hydrochloric acid.

*Euxanthine* crystallizes from its alcoholic solution in pale-yellow acicular crystals resembling those of berberine, of a sweetish-bitter taste, sparingly soluble in cold, but somewhat more abundantly in hot water: it is very soluble in boiling alcohol, but the greater part is again deposited as the solution cools. By the spontaneous evaporation of its solution in ether it is obtained in stellated acicular groups. Heated in the air it burns with a bright flame. By dry distillation a portion of it sublimes (*euxanthone*), and water and carbonic acid are evolved. Euxanthone is also formed by the dry distillation of the combinations of euxanthine with inorganic bases; and when euxanthine is dissolved in oil of vitriol, and the solution largely diluted with water, the substance which is precipitated appears to be euxanthone. If this sulphuric solution be not immediately diluted, it gradually becomes crystalline, and besides euxanthone, appears to contain a new acid. Euxanthine is also converted into euxanthone by hydrochloric acid gas.

Euxanthine is readily soluble in ammonia, potassa, and soda, forming yellow solutions, which yield crystalline compounds, soluble in water, but insoluble in solutions of the alkaline carbonates. When euxanthine is dissolved in a hot solution of carbonate of ammonia, potassa, or soda, carbonic acid escapes, and crystalline *euxanthates* are formed. These salts are soluble in alcohol. The solution of euxanthate of ammonia forms pale-yellow gelatinous precipitates with chloride of calcium and chloride of barium, which dissolve on boiling the liquor, but fall again as it cools: these compounds are gradually dissolved when washed with water.



*Euxanthate of magnesia* is the principal component of *purree*. When a solution of euxanthate of ammonia with excess of ammonia is mixed with a solution of chloride of magnesium and sal ammoniac, a bulky yellow precipitate is thrown down, which, on the application of heat, again dissolves, and afterwards falls in a crystalline form, and of an orange color, and is no longer soluble; as the liquor cools, it deposits deep yellow crystals, composed, according to Erdmann, of  $2 \text{ MgO} + \text{C}_{40} \text{ H}_{16} \text{ O}_{21}$ .

The solution of neutral euxanthate of ammonia precipitates most of the metallic salts of a yellow color, which precipitates are generally insoluble in the liquors from which they have been thrown down, but more or less soluble in pure water. The precipitates with the sulphates of zinc, manganese, and nickel, are pale yellow; with sulphate of copper, and nitrate of silver, the precipitates are yellow and gelatinous; the precipitate with protosulphate of iron is at first white, but soon blackens. Corrosive sublimate slowly yields a yellow precipitate.

The *euxanthate of lead* consists of  $\text{PbO}$ ,  $\text{C}_{20} \text{ H}_{16} \text{ O}_{21}$ ; there is also a *basic euxanthate of lead* obtained by adding an alcoholic solution of basic acetate of lead to a boiling alcoholic solution of euxanthine; its formula is  $2 \text{ PbO} + \text{C}_{40} \text{ H}_{16} \text{ O}_{21}$ . (ERDMANN.)

The following is the composition of *anhydrous euxanthine*:—

|                          |    |     |     |     |        | Erdmann. | Stenhouse. |
|--------------------------|----|-----|-----|-----|--------|----------|------------|
| Carbon .....             | 40 | ... | 240 | ... | 56.60  | ...      | 55.20      |
| Hydrogen .....           | 16 | ... | 16  | ... | 3.77   | ...      | 4.42       |
| Oxygen .....             | 21 | ... | 168 | ... | 39.63  | ...      | 40.38      |
| <hr/>                    |    |     |     |     |        |          |            |
| Anhydrous euxanthine.... | 1  |     | 424 |     | 100.00 |          | 100.00     |

*Euxanthone. Purrenone.* The production of this compound has been above described. Stenhouse obtained it by sublimation from impure euxanthine, in large crystals. When these contain euxanthine, it may be separated by digestion in a solution of carbonate of ammonia, in which euxanthone is insoluble. Euxanthone is but little soluble in cold water, alcohol, and ether, but abundantly soluble in boiling alcohol. It forms yellow solutions with the caustic alkalis. Its alcoholic solution has no acid reaction, and produces no precipitate in solution of chloride of calcium, chloride of barium, acetate of lead, and nitrate of silver. With subacetate of lead it yields a yellow precipitate. The components of euxanthone are

|                  |    |     |     |     |        | Stenhouse. | Erdmann. |
|------------------|----|-----|-----|-----|--------|------------|----------|
| Carbon.....      | 13 | ... | 78  | ... | 68.42  | ...        | 68.51    |
| Hydrogen .....   | 4  | ... | 4   | ... | 3.51   | ...        | 3.68     |
| Oxygen .....     | 4  | ... | 32  | ... | 28.07  | ...        | 27.81    |
| <hr/>            |    |     |     |     |        |            |          |
| Euxanthone ..... | 1  |     | 114 |     | 100.00 | 100.00     | 100.00   |

13. COLORING-MATTERS OF FLOWERS These are principally *blue*, (*Anthocyanine*); *red*, (*Antherythrine*); and *yellow*, (*Anthoxanthine*): they have as yet been imperfectly examined; many of them are very fugitive, and change considerably in tint, and are often altogether destroyed, on drying; others are comparatively permanent. According to Thomson, the expressed juice of most red flowers is blue, whence he infers that the coloring-matter in the petals is reddened by carbonic acid, which escapes on exposure. The violet is colored by a blue matter which is changed to



red by acids, and first to green, and then to yellow by alkalis, the green probably resulting from the mixture of blue and yellow. The petals of the red rose, when triturated with a little chalk and water, yield a blue liquor which is rendered green by alkalis and their carbonates, and restored to red by acids. The same blue coloring matter as that of the violet exists in many other flowers, and seems also to form the most usual *red* of the red flowers, in which it is apparently reddened by an acid, for many of these reds become blue, when cautiously neutralized by an alkali, and green and yellow by excess of alkali. This is also the case with the red of the red cabbage and of the radish. Some of these reds become blue, merely on being bruised, and give blue infusions with water, the reddening acid being probably carbonic acid, which escapes on the rupture of the cells or vessels. Schubler ascribes the red, orange, and yellow colors of flowers, to excess of oxygen; and the purple and blue colors, to deoxidizement. The color of yellow flowers is generally more permanent than that of the blue or red; it is usually rendered paler by acids, and deeper by alkalis. (THOMSON, *Veg. Chem.*, 386, 412, and 423. SMITHSON, *Phil. Trans.*, 1818. SCHUBLER, *Journ. de Pharm.*, xvi. 392.) The yellow coloring-matter of the flowers of the nasturtium, (*Tropæolum majus*) is readily soluble in water and in potassa, communicating a brownish-yellow color, which is changed to cherry-red by the acids, to greenish-blue by carbonate of soda, and to yellow and red, by several metallic salts. (JOHN, *Chem. Untersuchungen*, iii. 112.) The yellow coloring-matters of the flowers of the *Narcissus pseudonarcissus* have been examined by Caventou. (*Ann. Ch. et Ph.*, iv. 321.) Most of the coloring-matters of the petals of flowers are extremely susceptible of the bleaching influence of sulphurous acid. Marquart has endeavoured to show that the original coloring-matter of the petals is always *green*, in the bud, and that this is changed by the vital functions of the plant into two new coloring-matters, which are the origin of all others; one of these is blue, the other yellow: the blue he supposes to arise from the abstraction of the elements of water from the original green; and the yellow, from the addition of those elements. The coloring-matters of the petals may be extracted from them by digestion in weak alcohol, which leaves it on evaporation, generally in the form of colored extract: from *blue flowers* it is blue, violet, or purple, soluble in water and in proof-spirit, but insoluble in absolute alcohol, ether, and fat oils; it is reddened by acids, and a piece of zinc put into the red solution decolors it, but the color returns on exposure to air; basic substances change it to green. The coloring-matter of yellow flowers is partly soluble and partly insoluble in water and in spirit, and is rendered blue by sulphuric acid. The red petals of *Papaver rhæas* yield a red solution with lime water, or carbonate of soda; pure potassa renders it green; and hydrochloric acid, pale red. The color of red rose leaves is brightened by acids, and rendered green by alkalis.

14. COLORING-MATTER OF LEAVES. *Chlorophylline*. *Xanthophylline*. *Erythrophylline*. The substance from which leaves and herbage derive their green color, was first obtained in its pure state by Berzelius. It has been examined by Preisser, and by Mulder. (*Erdmann and Marchand's Journ.*, xxxii. 162, and xxxiii. 478.) It is procured by digesting the

crushed leaves (Berzelius used mulberry leaves) in renewed portions of ether; this tincture is then considerably evaporated on a water-bath, and the deposit which is formed is separated, dried, and treated with alcohol as long as green soluble matter is abstracted. The alcoholic solution is evaporated to dryness, and the residue digested in strong hydrochloric acid. The green hydrochloric solution is filtered, and mixed with water, by which the chlorophylline is precipitated; this precipitate is boiled in water, and afterwards dissolved in a strong solution of caustic potassa, which is then diluted, filtered, and precipitated by acetic acid; the precipitate, after having been washed and dried, is, according to Berzelius, pure chlorophylline. It seems, however, scarcely possible that these several agents should not somewhat have modified the matter originally existing in the leaves.

Chlorophylline appears as a dark-green earthy substance, which is grass-green when reduced to powder. It fuses at about  $390^{\circ}$ , and is insoluble in water. When moist, it is slightly soluble in alcohol, with a grass-green color; when dry, it is less soluble, and the color of the solution is bluish-green. It is similarly soluble in ether, and it communicates a green color to oil of turpentine and to fat oils. The formula assigned by Mulder to chlorophylline is  $C_{18}H_9O_8N$ .

When the ethereal solution of chlorophylline is long exposed to light, it acquires a yellow color, and on evaporation leaves a residue having all the characters of *xanthophylline*. Sulphuretted hydrogen has no action upon it when in hydrochloric or alkaline solution; but if a little zinc be introduced into its hydrochloric solution, and air excluded, the green color passes into yellow. On evaporating this yellow solution upon a water-bath, it reverts to green. Nitric acid dissolves a small portion of chlorophylline and renders it yellow. With concentrated sulphuric acid it produces a brilliant green solution, which, exposed to air, absorbs water, and the chlorophylline is precipitated. Hydrochloric acid, sp. gr. 1.14, dissolves chlorophylline of a deep emerald-color; chlorine first changes this green solution to yellow, and then bleaches it, with the separation of a portion of white matter. The chlorophylline may be entirely precipitated from its hydrochloric solution by the introduction of a piece of marble; or it may be obtained unchanged by evaporation. Cold acetic acid dissolves a very small portion of chlorophylline; when boiled, more is taken up, but it again falls as the solution cools.

The pure and carbonated alkalis entirely dissolve moist chlorophylline; but when it has been dried, a portion of insoluble matter always remains. The former solution is green, and precipitated by acetic acid. When the potassa solution is evaporated, it deposits *chlorophyllate of potassa*, soluble in pure water with a fine green tint. On evaporating the ammoniacal solution, pure chlorophylline remains. The potassa solution gives a fine green precipitate with solution of alumina. When the alcoholic solution of chlorophylline is added to acetate of lead, a grass-green precipitate falls, which is only partially decomposed when boiled with carbonate of potassa.

*Xanthophylline* is a term applied to the coloring matter extracted from the *yellow leaves* of autumn. It was obtained from the leaves of a pear-tree by Berzelius, by digesting them for several days in a bottle entirely filled with alcohol of sp. gr. 0.833, and well stopped, so as to



exclude air, for when air comes into the contact of the leaves under these circumstances, they change from yellow to brown. On distilling off the alcohol from the tincture thus prepared, and allowing the residue to cool slowly, the xanthophylline, together with a little resinous and fatty matter, is deposited. The fat may be removed by solution of potassa, and the remaining yellow matter then dissolved in alcohol, and mixed with an alcoholic solution of acetate of lead; a slight precipitate falls, from which the alcoholic liquor must be poured off; the lead is then precipitated by hydrochloric acid, water added, and the alcohol distilled off; the xanthophylline then separates in the form of a dark yellow fat-like substance, fusible at about  $110^{\circ}$ , and becoming transparent on cooling; it is insoluble in water, sparingly soluble in alcohol, and readily soluble in ether. It is very sparingly soluble in solution of caustic potassa, and the solution soon loses its yellow color when exposed to light.

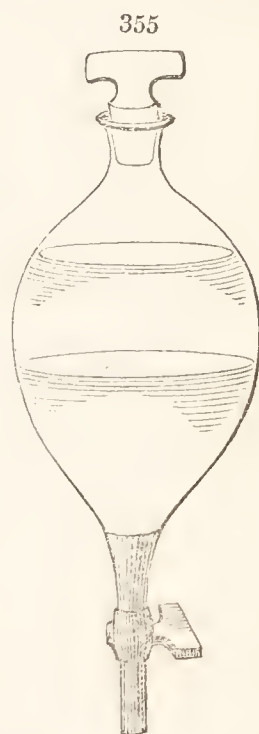
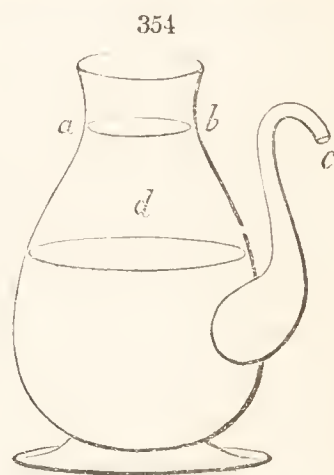
*Erythrophylline.* It has been remarked by Berzelius that all trees and shrubs the leaves of which redden in autumn, bear red fruit or berries. (*Sorbus aucuparia*, *Prunus cerasus*, *Ribes*, *Grossularia*, &c.) He obtained this red coloring-matter from cherry and red currant leaves, by digesting them, when in the proper condition, in alcohol, and distilling the red tincture; water was added to the residue, and the mixture filtered to separate precipitated fat and resin; solution of acetate of lead was then added to the clear filtrate as long as a brown precipitate was formed, which was washed, and decomposed by sulphuretted hydrogen. The sulphuret of lead was separated on a filter, and the filtrate evaporated to dryness: the erythrophylline remained in the form of a red extract. Exposed to air it easily passes into a brown substance, insoluble in water. Its combinations with bases are of a grass-green color; if therefore the red leaves be digested in alkalis, the resulting solutions are green; but acids reproduce the red color. Under the influence of alkalis this coloring matter speedily passes into the same brown state, which it also acquires by exposure to air only. An alcoholic solution of erythrophylline remains however long unchanged, even in a half-filled bottle. The changes of color which the leaves of many forest trees undergo in autumn, passing from green to red, and from red to yellow, have been ascribed by Macaire-Prinsep to the action of certain chemical agents upon a single coloring-matter. (*Ann. Ch. et Ph.*, xxxviii. 415.) But L. Gmelin has remarked, that chlorophylline is not rendered yellow by acids, nor xanthophylline red: and the statement above given respecting the properties of chlorophylline, seems to show that it is not in itself susceptible of such changes of color. (BERZELIUS, *Lehrbuch*. L. GMELIN, *Handbuch*. LÖWIG, *Chem. d. Org. verbind.*)

## § XII. ESSENTIAL OILS. CAMPHORS.

THE *essential* or *volatile oils* may be regarded as the odorous principles of vegetables, and the term is generally applied to these products, as obtained by distilling the plant with water; in some cases the oil is thus derived from the fresh or salted plant, as from roses, and orange flowers; in others from the dried plant; and sometimes it may be pressed out of the cellular structure containing it, as in orange and lemon peel. These oils



are frequently obtained from every part of the plant, but there are generally peculiarities in the oil derived from different parts of the same plant; thus with regard to the orange-tree, the leaves, flowers, and fruit, each yield a distinct oil. The boiling-points of almost all these oils are above that of water, but their vapors are carried over with steam at  $212^{\circ}$ , and condensed with it in the refrigerator; a portion of the oil is however always retained in solution in the water, constituting the medicated and perfumed waters, while the remainder either floats upon the surface or sinks to the bottom, according as it is less or more dense than distilled water. The greater number of these oils are lighter than water, and in such cases the distilled product is received into a vessel of the annexed form (fig. 354), in which, when the water has reached the level *a, b*, it runs off by the pipe *c*, whilst the oil floats upon its surface, and ultimately fills the space *d*. The whole contents of the recipient are then poured into a funnel, the tube of which is closed by the finger, and, when the oil has collected upon the surface, the water is suffered to run from beneath it, and the oil transferred into a bottle. When the oil is heavier than water, these operations are of course inverted. Instead of a common funnel, the *separator*, shewn in fig. 355, is often employed, and is more convenient, as the oil may be retained in it, and at the same time preserved from contact of air. The distilled water, being in these cases already saturated with the oil, should be retained for a repetition of the distillation. The produce of oil is sometimes stated to be increased by adding salt to the water in the still, so as to elevate its boiling-point. When, as in the case of oranges, lemons, and similar fruits, the oil is expressed instead of distilled, the yellow part of the rind is rasped off and pressed in hair-cloth bags; the expressed juice separates on standing, into two distinct portions, the inferior of which is aqueous, and the superior oily. The oil thus obtained is generally more fragrant than when heat has been resorted to, but it is at the same time less pure; and although it gradually clarifies itself by depositing the substances held in mechanical suspension, it retains coloring and other matters in permanent solution, so that when dropped upon paper it leaves a stain, and does not produce a clear alcoholic solution. There are some of these oils which are produced in such small quantities, or which are so delicate and evanescent, as not to admit of collection by either of the preceding methods, such as the fragrancy of the flowers of jasmine, of the violet, the tuberose, the lime tree, the narcissus, and some others. To obtain these, the fresh flowers are stratified with layers of cotton imbued with some inodorous fixed oil; this gradually absorbs the volatile oil or perfume of the flower, and when saturated with it, the cotton is digested in alcohol, which abstracts the essential from the fixed oil, and an odoriferous *essence* is obtained. Sometimes the cotton is distilled with water or with alcohol, and the oil separated by that process; it is, however, generally too





delicate to admit of such treatment without great deterioration, or even entire destruction.

The essential oils are applied to many useful purposes; those which are most abundant, and therefore cheapest, are used in the manufacture of paints and varnishes, and even occasionally burned in lamps; others are employed in pharmacy and medicine, and are generally powerful and diffusible stimulants; others, and especially such as possess agreeable odors, are used for the various purposes of perfumery. In general, these oils are ready formed in the plants whence they are derived; but in some cases they are no doubt generated by the action of water upon peculiar principles existing in the vegetable, as in the remarkable case of the production of bitter-almond oil, the details of which have been given above (p. 1378), and in a few others afterwards to be noticed. Hence also some plants which are naturally inodorous, yield a strongly scented volatile oil after they have been subjected to fermentation, as in the case of the *lesser centaury* (*Centaureum minus*). There are also a few instances in which essential oils have been artificially produced, as that of the *spiræa* oil, by the oxidizement of salicine (p. 1382); and one or two others afterwards to be noticed.

The essential oils are mostly colorless, or nearly so, when fresh and pure, but they generally are of various tints of yellow and brown, or soon become so under the influence of air; some few of them are green and blue, and several of them, even after having acquired color, lose it under the continuous influence of light. Their odors more or less resemble those of the fresh plants whence they are derived, but are less agreeable, partly in consequence of concentration, for they become more pleasant when diluted by, or diffused through, a large bulk of air, or when attenuated by solution in some inodorous vehicle.

Liebig has observed that the odor of these oils is greatly influenced by their chemical relations to air and water; that they all absorb oxygen; and that those which do so most rapidly, are most odorous. If non-oxygenised oils (hydrocarbons) be distilled off quicklime, either *in vacuo* or in a stream of carbonic acid, the product is so far inodorous that it is difficult, under these circumstances, to distinguish oil of lemons, of juniper, and of turpentine, from each other; but, after exposure to air, especially if spread upon a piece of paper, their natural characteristic odors return, and they at the same time become viscid and resinous; so that it would appear as if the odor was the result of the act of oxidizement, as is the case with metallic arsenic.

They are almost all possessed of strong, aromatic, and often extremely pungent and burning flavors, and many of them are poisonous. They have not the greasy feel of the fat oils, but, on the contrary, are rather rough upon the cuticle, and cause a cork moistened by them to squeak when twisted into a phial. They are inflammable, and burn with a bright, but often very fuliginous flame.

The specific gravity of the essential oils fluctuates between the extremes of 0.846 and 1.097. The greater number of them are lighter than water, as shown in the following table of their average specific gravities; but the results can only be considered as approximate, for the densities appear to vary with the mode of distillation, and the period of that process at which they are collected, the first portions which pass

over being often less dense than the last. They are also influenced by the condition of the plant, the period at which it is cropped, the age of the oil, and its greater or less exposure to air; so that the same kind of oil produced in England, and elsewhere, often varies considerably. Thus Proust found camphor in the oils of some of the *labiatæ* of Spain, while there was none in those of France.

## SPECIFIC GRAVITIES OF THE ESSENTIAL OILS.

|  |                  |
|--|------------------|
| Oil of aniseed (English) .....                 | 0·9868           |
| „ „ (Foreign) .....                            | 0·9903           |
| „ bergamot .....                               | 0·850            |
| „ cajaputi .....                               | 0·9263           |
| „ caraway .....                                | 0·9310 to 0·94   |
| „ cassia .....                                 | 1·071            |
| „ chamomile (English; from flowers only) ..... | 0·9083           |
| „ „ (Foreign) .....                            | 0·9289           |
| „ cinnamon .....                               | 1·036            |
| „ cloves .....                                 | 1·034 to 1·052   |
| „ copaiva .....                                | 0·878            |
| „ cubebs .....                                 | 0·929            |
| „ cumin .....                                  | 0·860            |
| „ dill .....                                   | 0·994            |
| „ elemi .....                                  | 0·849            |
| „ fennel .....                                 | 0·997            |
| „ juniper (English) .....                      | 0·8688           |
| „ „ (Foreign) .....                            | 0·8834 to 0·9110 |
| „ lavender (English, from flowers only) .....  | 0·8960           |
| „ „ (English, from the whole herb) .....       | 0·9206           |
| „ lemon peel .....                             | 0·8569           |
| „ marjoram .....                               | 0·9090           |
| „ nutmegs .....                                | 0·9480           |
| „ orange peel .....                            | 0·8880           |
| „ pennyroyal .....                             | 0·9390 to 0·9780 |
| „ pepper .....                                 | 0·8640           |
| „ peppermint (English) .....                   | 0·9070           |
| „ pimenta .....                                | 1·021            |
| „ rosemary .....                               | 0·9118           |
| „ rue .....                                    | 0·8670           |
| „ sassafras .....                              | 1·094            |
| „ spearmint .....                              | 0·9394           |
| „ spike lavender .....                         | 0·9360           |
| „ turpentine .....                             | 0·870            |

The greater number of the volatile oils appear to be mixtures of two, and sometimes of three, different products, one of which is a *hydrocarbon*, and the other an *oxyhydrocarbon*; and in many cases the latter, when isolated, assumes a concrete form, constituting a species of *camphor*. Berzelius applies the terms *stearoptene* and *elaioptene* to these solid and fluid products; (from *στέαρ*, *fat*, or *ελαιον*, *oil*, and *πτηνός*, *volatile*), and they often admit of separation by the application of cold, which causes the camphor to solidify; or by distillation, when the portion of the oil which is destitute of oxygen passes over at a lower temperature than that which contains oxygen; but when these mixed oils are thus distilled, their separation is never perfect, the more volatile hydrocarbon always carrying over with it a portion of the less volatile oxyhydrocarbon; so that other methods are resorted to, entirely to deprive the former of oxygen, amongst which, the action of fused caustic potassa is one of the



most efficient, for by it the whole of the oxygen (and part of the carbon) is abstracted in the form of carbonic acid. This variable composition of the essential oils explains the inequality of their boiling-points; but frequently the cause of the rise of the thermometer during the progress of distillation depends upon a progressive decomposition of the oil, in which case more or less gas is generally evolved. Although nearly all these oils are, as just stated, constituted either of carbon and hydrogen, or of carbon, hydrogen, and oxygen, there are a few which contain sulphur and nitrogen, but these are of a very peculiar character, and will be separately noticed.

It has already been mentioned that the essential oils are dissolved, though in small quantity, by water, to which they communicate taste and odor, and the London Pharmacopœia directs the extemporaneous preparation of several of these waters, by adding the oil, (subdivided by trituration with a little carbonate of magnesia,) to simple distilled water, instead of distilling the water off the herb itself: a little alcohol is also directed to be added to the water, with a view of preserving it from change; but Warrington has shown, that alcohol has the opposite effect, and that distilled waters which keep well without such addition, are liable to acetification with it. (*Mem. Chem. Soc.*, ii. 261.) Some of these oils apparently enter into chemical combination with definite proportions of water to constitute crystallizable compounds, or camphors. They dissolve abundantly in absolute alcohol, and in ether.

Exposed to the influence of oxygen, or air, the volatile oils undergo two distinct series of changes; some of them seem directly to combine with oxygen to form crystallizable, and, in many cases, acid compounds, as in the cases of bitter-almond oil, and cinnamon oil, already noticed, (pp. 1357, 1390,) and others which remain to be mentioned. But, in other cases the action of air changes the oil into a resinous substance, a portion of its hydrogen being probably converted into water, so as to leave excess of carbon in the residue.

The action of chlorine upon many of these oils is attended by the immediate production of hydrochloric acid, and compounds of chlorine, and of hydrochloric acid, with the remaining elements of the oil, are formed. The same happens with iodine and with bromine; and in some cases the decomposition of the oil thus effected is so intense as to give rise to inflammation. The action of acids, and other agents, vary considerably with the nature of the oil; the action of nitric acid is also for the most part intense, and frequently attended by the formation of a resinoid product.

Amongst the essential oils which are destitute of oxygen, (the hydrocarbons, namely, of the series) there is a remarkable identity of composition; they contain between 88 and 89 *per cent.* of carbon, and between 11 and 12 *per cent.* of hydrogen, proportions which are expressed by the formula  $C_5H_4$ ; so that their varieties may be generally regarded as isomeric or polymeric modifications of a hydrocarbon so constituted; being, namely,  $C_5H_4$ , or  $C_{10}H_8$ , or  $C_{20}H_{16}$ , or  $C_{40}H_{32}$ , points which are best determined by the respective densities of their vapors, it being obvious that in respect to the equivalent, or atomic weight of the compound, as deduced from its combinations, it may be represented as  $C_5H_4$  or  $2[C_5H_4]$ ,  $3[C_5H_4]$ ,  $4[C_5H_4]$ , &c. In some cases these isomeric



modifications only admit of distinction by their action upon polarized light, some of them rotating the ray to the *right*, others to the *left*, and others transmitting it uninfluenced; showing that although there is identity of composition, of atomic weight, and even of density of vapor, there is, nevertheless, a difference in what may be termed their *molecular constitution*.

In consequence of the high price of many of these oils, they are subjects of various adulterations, sometimes with alcohol and with fixed oils, and sometimes with the cheaper essential oils.

When *alcohol* is used, it may generally be separated by agitating the adulterated oil with water, or with a saturated solution of common salt, and its quantity appreciated by the diminution of bulk which the oil so treated sustains: this falsification is also indicated by a slight increase of temperature when the oils are mixed with water, and which is not observed when they are pure. Alcohol may also be abstracted from an essential oil by means of fused chloride of calcium. The volatile oils, when pure, dissolve perfectly in all proportions in the fixed oils, without interfering with their transparency; but not so when the former are adulterated with alcohol: in that case, a few drops of the adulterated oil added to a perfectly transparent fixed oil, produces more or less turbidness.

The admixture of a *fixed oil* is ascertained by the greasy stain which remains when a drop of the oil is evaporated before the fire from a piece of bibulous paper; but some of the genuine essential oils, especially such as are old, or have been exposed to air, often under these circumstances leave a stain, which however is rather resinous than greasy. When an essential oil thus adulterated is rubbed between the finger and thumb, it generally has more or less of a distinct greasy feel; or if distilled with water, the fixed oil remains behind; if mixed with about thrice its bulk of alcohol, of sp. gr. 0.84, the fixed oil is also separated.

The adulteration of a *high-priced* with a *cheaper essential oil* is more difficult of detection, and requires for its discovery a practical acquaintance with the odor, flavor, and other distinctive characters of the genuine oil, which can only be attained by experience. When oils are falsified with oil of turpentine, its characteristic odor is often covered, till the adulterated oil is dissolved in a little alcohol, and the solution mixed with water, when both the odor and flavor of the turpentine become manifest. The refractive indices of the adulterated oils generally differ from those of the genuine article, and many years ago Dr. Wollaston suggested a form of instrument for their determination, (*Phil. Trans.*, 1802,) which has been improved by Mr. Cooper, (*Mem. Chem. Soc.*, i. 234): it is often useful, but the refractive power of the genuine oil varies too much to render it satisfactorily available.

The essential oils are very numerous and many of them have been examined in great detail, and have given rise to a long list of new compounds and derivatives, of which the most important only can be here noticed. For the purpose of chemical description, they may conveniently be arranged into four classes, namely: 1. Essential oils composed of carbon and hydrogen only. 2. Essential oils composed of carbon, hydrogen, and oxygen. 3. Camphors, or concrete essential oils. 4. Essential oils containing nitrogen and sulphur.



I. ESSENTIAL OILS CONTAINING CARBON AND HYDROGEN ONLY.  
VEGETABLE HYDROCARBONS.

**OIL OF TERPENTINE. CAMPHENE. CAMPHYLE.** This product, known also under the name of *spirit* or *essence* of *terpentine* or *turpentine*, and called in commerce, *terps*, is derived from the semifluid resinous exudation which flows from the wounded bark of trees belonging to the *Coniferae*, or *fir* tribe, especially from the genus *Pinus*; it is commonly known under the name of *Terpentine*, and is a mixture of resin and the volatile oil; a kind of *balsam* therefore. The oil is separated by distilling the terpentine with water, along with the vapor of which it passes over and is afterwards condensed, leaving the resin behind in the still.

According to Pereira (*Mat. Med.*, p. 1043) the oleo-resinous exudations of the coniferous terebinthines, constituting the various *terpentines*, are originally liquid, and become more or less viscid, or even solid, partly by the volatilisation and partly by the resinification of the volatile oil. They have a general similarity in taste and odor; soften, and liquefy by heat; and burn with a white flame, and copious deposition of finely-divided carbon (*lamp black*); they are almost completely soluble in alcohol and in ether; and yield, by distillation, a volatile oil which passes over (usually with a small quantity of succinic acid?) and a resinous residuum: the following are their principal varieties.

1. *Common terpentine*, obtained from different species of *Pinus*. The London market is almost exclusively supplied with this article from New York, a small quantity only being imported from Bourdeaux. 2. *Venice, Strasburgh, Swiss, or larch terpentine*, obtained from the *Larix Europæa*. It is characterised by its slight tendency to thicken or solidify. The article usually sold under this name is factitious, and made by fusing a pound of resin with about 5 ounces of oil of terpentine. 3. *Canadian terpentine*, or *Canada balsam*, obtained from *Abies balsamea*, in Canada, and the State of Maine; when fresh it is of the consistence of honey, but gradually solidifies; it is yellow and transparent, its odor agreeable, and its taste bitterish. 4. *Common frankincense*, which is the spontaneous exudation of *Abies communis*; it concretes into yellow drops or tears.

*Oil of terpentine* is obtained by distilling American terpentine, previously melted and strained, with a due proportion of water, the average product amounting to from 14 to 16 *per cent*. Bourdeaux terpentine yields an inferior oil and resin. It is purified by redistillation from a solution of caustic potassa, and in this state comes into the market under the name of *rectified oil of terpentine* and *camphene*. To render it perfectly pure, it requires to be redistilled with water, and again off chloride of calcium.

Thus purified, oil of terpentine is a limpid, colorless liquid, of a peculiar and somewhat unpleasant odor, and a hot taste; its sp. gr. is 0.86 to 0.87 at 60°; its boiling-point is about 314°, and the density of its vapor 4.76. It is neutral to test paper; almost insoluble in water; and only soluble to a small extent in hydrated alcohol. 100 parts of alcohol, sp. gr. 0.840, dissolve between 13 and 14 parts; by absolute alcohol it is taken up in larger proportion, as also by ether. It mixes readily with the fixed oils. When a piece of paper or cotton dipped in oil of terpentine, is set fire to, it burns energetically, with a large

sooty flame ; but if burned in a properly constructed lamp, with a due supply of air, it gives an extremely brilliant and smokeless light, and may be burned to dryness. The oil used for this purpose should be of the purest kind, and freshly distilled, and the canisters in which it is kept should be carefully stopped, so as effectually to exclude air ; for after it has been for some time exposed to air, it no longer burns with the same facility and perfection, but is apt to smoke, and clog the wick : for the same reason the oil should never be long left in the lamp, but entirely burned out of the reservoir as frequently as possible. It is also requisite for the due performance of these lamps, that the oil in the reservoir should not become heated ; in the best constructed lamps, therefore, a *non-conductor of heat* is so interposed between the flame and the oil-holder, as to cut off the communication of heat from the former to the latter. A pint of good oil of terpentine burns in one of these Argand lamps for about ten hours, and gives the light of about twelve spermaceti candles. The great inflammability of oil of terpentine renders it dangerous when kept in quantity ; and if preserved in wooden casks, they are apt to leak ; so that they are generally placed within another cask or barrel, filled with water.

The components of oil of terpentine, assuming its equivalent to be 68, are

|                   |       |      |       |      |        | Dumas. | Blanchet<br>and Sell. |      | Wöhler. |      |       |
|-------------------|-------|------|-------|------|--------|--------|-----------------------|------|---------|------|-------|
| Carbon .....      | 10    | .... | 60    | .... | 88·23  | ....   | 88·4                  | .... | 88·6    | .... | 88·3  |
| Hydrogen.....     | 8     | .... | 8     | .... | 11·77  | ....   | 11·6                  | .... | 11·4    | .... | 11·7  |
| <hr/>             | <hr/> |      | <hr/> |      | <hr/>  |        | <hr/>                 |      | <hr/>   |      | <hr/> |
| Oil of terpentine | 1     |      | 68    |      | 100·00 |        | 100·0                 |      | 100·0   |      | 100·0 |

When oil of terpentine is distilled over the open fire, its rotatory power in relation to polarized light is increased ; if, on the other hand, it be subjected to a higher temperature, by distilling it off pulverised brick, its rotatory power is diminished ; its specific gravity is also reduced from 0·87 to 0·84 ; and in this state, its solvent power over caoutchouc is considerably augmented.

When the vapor of oil of terpentine and humid carbonic acid gas are slowly passed together through a tube heated to dull redness, water and carbonic oxide are the results, together with a hydrocarbon, = C<sub>10</sub> H<sub>7</sub>. (C<sub>10</sub> H<sub>8</sub> + CO<sub>2</sub> ; = C<sub>10</sub> H<sub>7</sub> + CO + HO.) It has already been stated, that under the continuous influence of oxygen, oil of terpentine acquires a resinous consistence, and, in fact, passes ultimately into water and colophony. (4[C<sub>10</sub> H<sub>8</sub>] + O<sub>6</sub> = C<sub>40</sub> H<sub>30</sub> O<sub>4</sub>, (*colophony*) + 2HO.) According to Weppen and Laurent, a portion of formic acid is generally found in common oil of terpentine (*Ann. der Pharm.*, xli. 294), and is formed, along with resin, when the oil is exposed to air.

*Hydrates of Oil of Terpentine. Terpentine-Camphors.* When oil of terpentine which has been agitated with water is kept for some time at a temperature of 120°, crystals gradually form in it, composed of C<sub>10</sub> H<sub>8</sub> + 2HO. (BLANCHET and SELL, *Journ. de Pharm.*, xx. 224.) When oil of terpentine and water are left together at common temperatures, crystals are gradually formed at those points at which the drops of water and oil are in contact, composed of C<sub>10</sub> H<sub>8</sub> + 3HO. (DUMAS and PELIGOT, *Ann. de Chim.*, lxvii. 334.) Hertz has also described similar



hydrates. (*Poggend. Ann.*, xliii. 190.) According to Wiggers (*Ann. der Pharm.*,) hydrate of oil of terpentine is most abundantly formed when 8 parts of the oil, 2 of nitric acid of sp. gr. 1.25 to 1.30, and 1 part of alcohol, sp. gr. 0.845, are repeatedly shaken together for two or three days, till crystals begin to appear: the mixture is then set aside, and if kept at a temperature of about  $70^{\circ}$ , a considerable quantity of the crystals separates, for about 14 days: they are also  $C_{10}H_8 + 3HO$ . These hydrates are frequently termed *camphors*, and several others have been described by the authorities above quoted.

*Action of Chlorine, Bromine, and Iodine, upon Oil of Terpentine.* When excess of *chlorine* is passed through oil of terpentine, a viscid, colorless liquid is produced, having a peculiar camphoric odor, and sweetish-bitter taste. It consists, according to Deville, of  $C_{10}H_6Cl_2$ , and is peculiar in rotating the polarised ray to the *right*. By the action of *bromine* on the oil, a corresponding compound,  $= C_{10}H_6Br_2$ , is produced; it is of a dark-red color, and appears from Deville's statement, also to rotate to the *right*. (*Ann. Ch. et Ph.*, lxxv. 60.) Oil of terpentine dissolves *iodine*, forming a dark-green solution. When excess of iodine is added to oil of terpentine, a brown compound is obtained, and hydriodic acid evolved: if the terpentine oil be warm, the action is violent: so also if a piece of bibulous paper, imbued with warm oil of terpentine, be plunged into a jar of chlorine, it fumes, blackens, and generally inflames.

*Hydrochlorate of Oil of Terpentine. Kind's Artificial Camphor.*  $2[C_{10}H_8] + HCl = C_{20}H_{17}Cl$ . This compound was discovered by Kind, (*Ann. de Chim.*, li. 270,) and has been the subject of much subsequent investigation. It is formed by slowly passing dry hydrochloric acid gas through oil of terpentine in a vessel surrounded by ice, so as to keep down the temperature, which would otherwise increase so as to prevent the absorption of the gas; when this no longer takes place, the liquor is set aside in a cool situation, where it gradually deposits white crystals, the mother-liquor being brown and fuming. The amount of the product varies considerably; according to some, the oil furnishes not more than one-fourth of its weight; others have obtained from one-third to one-half; and according to Thenard, (*Mem. d'Arcueil*, ii. 26,) 100 parts of oil afford 110 of crystals. Blanchet and Sell ascribe these differences in the weight of the product, to peculiarities in the composition of different samples of oil of terpentine, which they say contains *two isomeric oils*, one of which forms a *solid*, and the other a *liquid* compound, with hydrochloric acid.

The crystalline compound forms white prisms having an odor resembling that of ordinary camphor, and an aromatic flavor; it fuses at  $240^{\circ}$ , and boils at  $330^{\circ}$ . It is insoluble in water; alcohol of sp. gr. 0.806, at  $55^{\circ}$ , dissolves it to the amount of one-third of its weight, and it is precipitated on the addition of water. Its ultimate elements are

|   | Dumas. |      |     |      |        |      | Blanchet and Sell. |            |
|---|--------|------|-----|------|--------|------|--------------------|------------|
| Carbon.....                                   | 20     | .... | 120 | .... | 69.36  | .... | 70.0               | .... 70.20 |
| Hydrogen .....                                | 17     | .... | 17  | .... | 9.82   | .... | 9.7                | .... 10.01 |
| Chlorine .....                                | 1      | .... | 36  | .... | 20.82  | .... | 20.3               | .... 19.79 |
| <hr/>   |        |      |     |      |        |      |                    |            |
| Hydrochlorate of oil }<br>of terpentine ..... | 1      |      | 173 |      | 100.00 |      | 100.0              | 100.00     |

When the preceding hydrochlorate is decomposed by repeatedly distilling it off quicklime, chloride of calcium and water are formed, together with a peculiar oil, isomeric with oil of terpentine,  $\text{C}_{10}\text{H}_8$ , and which has received various names; it has been called *dadyle* (*δαδῖον a torch*, from *δαῖω to burn*) by Blanchet and Sell; *terebene*, by Soubeiran and Capitaine; and *camphilene* by Deville. This compound has no rotatory power; its sp. gr. is 0·87, and its boiling-point  $293^\circ$ . Chlorine, and hydrochloric acid, act upon it as on oil of terpentine. Nitric acid gradually converts it into a yellow crystalline substance which combines with bases.

When the brown *liquid hydrochlorate of oil of terpentine*, from which the crystalline hydrochlorate has been separated, is decomposed by distillation from quicklime, another distinct, but also isomeric product ( $\text{C}_{10}\text{H}_8$ ) is obtained, which has been called *terebilene* by Deville, and *peucile* by Blanchet and Sell (from *πευκη a fir tree*.) It has no rotating power; its specific gravity is 0·86, and the density of its vapor 4·787; but its boiling-point is as low as  $272^\circ$ .

It appears, therefore, that there are three isomeric conditions of oil of terpentine, namely, 1, *ordinary oil*; 2, *dadyle*; and 3, *peucile*; but it is not improbable that the ordinary oil is in fact a mixture of the two last-mentioned modifications, and that its varying properties may be partly ascribed to the predominance of one or other of those component hydrocarbons.

*Hydriodate of Oil of Terpentine*,  $2[\text{C}_{10}\text{H}_8] + \text{HI}$ , is obtained when hydriodic acid gas is passed into the oil; it forms a thick, dark-red fuming compound, which when freed from excess of acid by means of chalk, and of water by chloride of calcium, shows no tendency to crystallize. It may be deprived of color, which arises from its holding a little free iodine in solution, either by weak alcohol, mercury, or weak solution of potassa; it then has an agreeable camphoric odor: its sp. gr. at  $60^\circ$  is 1·5097. It speedily reddens, and even becomes black when exposed to air. (DEVILLE, *An. Ch. et Ph.*, LXXV, 55.) Its ultimate components appear to be

|                                     |    |     |     |     | Deville. |        |
|-------------------------------------|----|-----|-----|-----|----------|--------|
| Carbon .....                        | 20 | ... | 120 | ... | 45·62    | 45·99  |
| Hydrogen .....                      | 17 | ... | 17  | ... | 6·46     | 6·35   |
| Iodine .....                        | 1  | ... | 126 | ... | 47·92    | 47·66  |
| <hr/>                               |    |     |     |     |          |        |
| Hydriodate of oil of terpentine.... | 1  |     | 263 |     | 100·00   | 100·00 |

*Hydrobromate of Oil of Terpentine*,  $2[\text{C}_{10}\text{H}_8] + \text{HBr}$ . When hydrobromic gas is passed into the oil, a dark-colored fuming liquor is formed, which when cooled down to  $32^\circ$ , deposits crystals, the weight of which exceeds that of the original oil; they may be purified and rendered colorless, first by pressure, and then by crystallization from alcohol. The alcoholic solution of this substance reddens when exposed to air, in consequence of the liberation of a portion of bromine. The components of this hydrobromate are

|  |    |     |     |     | Deville. |        |
|--|----|-----|-----|-----|----------|--------|
| Carbon .....                           | 20 | ... | 120 | ... | 55·82    | 56·07  |
| Hydrogen .....                         | 17 | ... | 17  | ... | 7·90     | 7·94   |
| Bromine.....                           | 1  | ... | 78  | ... | 36·28    | 35·99  |
| <hr/>                                  |    |     |     |     |          |        |
| Hydrobromate of oil of terpentine .... | 1  |     | 215 |     | 100·00   | 100·00 |



*Terebene.* This distinctive term has been applied by Deville to a product isomeric with oil of terpentine, camphene, &c., which is most easily procured by the action of concentrated sulphuric acid upon oil of terpentine; but other chemists have designated all the hydrocarbons represented by  $C_{10}H_8$  as *terebene*; hence Löwig has termed the particular product now under consideration, *tereбен*. The oil and the acid should be carefully mixed, and not in too large quantities, in case of inflammation; the heat evolved is sufficient to commence the distillation, which may afterwards be continued in a sand-heat, and all the products collected which pass over at a temperature below  $400^{\circ}$ . Above that temperature, *colophene* is evolved. Sulphurous acid is formed during the whole process. The liquor which is in the receiver must be repeatedly treated with sulphuric acid in the same way, for the purpose of acting upon any unchanged oil of terpentine, and ultimately deprived of sulphurous acid by carbonate of potassa, and of water by chloride of calcium. No chemical rule can be laid down for ascertaining when the change into terebene is complete; it can only be judged of by the disappearance of all rotatory power in respect of polarized light. Deville prefers this process, for the preparation of terebene, to that above-mentioned, in which the liquid product resulting from the action of hydrochloric acid upon oil of terpentine is rectified over quicklime and chloride of calcium, inasmuch as in the latter case the absence of a portion of the camphor in solution can never be ensured.

Terebene, when pure, has a distinct odor from that of oil of terpentine; it resembles that of thyme, and may therefore be applicable in certain cases where the disagreeable odor of the original oil is an objection to its use. The composition, specific gravity, boiling-point, and density of the vapor of terebene, are in all respects the same as those of oil of terpentine.

*Combinations of Terebene with the Hydracids.* Terebene combines in two proportions with the hydracids. Thus, with *hydrochloric acid* it forms  $4[C_{10}H_8] + HCl = C_{40}H_{33}Cl$ ; and  $2[C_{10}H_8] + HCl = C_{20}H_{17}Cl$ . The *first* of these compounds, (called by Deville *monochlorhydrate of terebene*) is obtained by the direct combination of hydrochloric gas with terebene; it is an extremely thin liquid, having a mixed odor of terpentine and camphor; its sp. gr. at  $68^{\circ}$  is 0.902; it is constituted by 4 volumes of the vapor of terebene with 2 of hydrochloric gas. The *second* compound is the liquid residue of the preparation of artificial camphor. There are also two corresponding *hydriodates*, and two *hydrobromates*. (DEVILLE, *Ann. Ch. et Ph.*, LXXV. 44.)

*Colophene.*  $C_{20}H_{16}$ . This hydrocarbon is one of the results of the distillation of oil of terpentine with sulphuric acid. In this process, after the production of terebene by distillation below  $400^{\circ}$ , the heat is raised till the viscid substance in the retort boils, when a thick yellow oil passes over, which, when redistilled several times by itself, and ultimately, to free it from sulphur, once off an alloy of potassium and antimony, is a colorless liquid when simply viewed by transmitted light; but when the phial containing it is a little raised, and a dark substance held behind it, so as diminish the quantity of transmitted light, the colophene then exhibits a species of dichroism, showing a tint of dark indigo-blue. This double color may be recognized in almost all the solutions of colo-

phene. The specific gravity of colophene at  $48^{\circ}$  is 0.940, and at  $76^{\circ}$ , 0.9394. It is isomeric with oil of turpentine. Its boiling-point is between  $590^{\circ}$  and  $600^{\circ}$ . The density of its vapor appears to be 9.5, = double that of the vapor of oil of turpentine. It has a peculiar odor, and no power of rotation. It absorbs chlorine, and produces a resinoid substance. It also absorbs hydrochloric gas, but the compound is decomposed by chalk.

*Succinone* (p. 1393) and *petrolene*, a substance contained in certain bitumens, in combination with asphalt, (BOUSSINGAULT, *Ann. Ch. et Ph.*, LXIV. 146) are isomeric with colophene.

*Terebinic Acid*.  $C_{14}H_9O_7 + HO$ . This acid is obtained by cautiously adding oil of turpentine by very small portions at a time, to nitric acid heated to about  $130^{\circ}$ , till nearly, but not quite the whole of the acid is decomposed. The action is extremely violent, and a resinous matter is formed, which, by heating the liquor to its boiling-point, is dissolved; on cooling, the clear liquor is mixed with water, by which the resin is precipitated, and when removed, the remainder is evaporated to the consistence of syrup, and set aside. After some time, it deposits small prismatic crystals of *terebinic acid*; they have a sour taste, and consist, according to Bromeis (*Ann. der Pharm.*, xxxvii. 292,) and Rabourdin, (*Journ. de Pharm.*, Nouv. Sér., vi. 185) of

|                             |    |     |     |     |        | Bromeis. | Rabourdin. |
|-----------------------------|----|-----|-----|-----|--------|----------|------------|
| Carbon .....                | 14 | ... | 84  | ... | 53.16  | ...      | 53.18      |
| Hydrogen .....              | 10 | ... | 10  | ... | 6.33   | ...      | 6.25       |
| Oxygen .....                | 8  | ... | 64  | ... | 40.51  | ...      | 40.57      |
| Crystallized terebinic acid | 1  |     | 158 |     | 100.00 |          | 100.00     |

**OIL OF LEMON. CITRENE.**  $C_{10}H_8$ . This oil is, as above stated, obtained both by expression and by distillation. The former, called also *oleum de cedro*, is the more fragrant; the latter clearer, and keeps better: it is sold under the name of *scouring drops*, and used to remove grease stains from silk, &c. This oil is chiefly imported from Portugal, Italy, and the south of France. It is very fluid; of an agreeable lemon-odor; and when pure, colorless. Its flavor is pleasant but pungent, and it is often used by cooks and confectioners as a substitute for lemon-peel; the flavor, however, which it thus communicates frequently savors of turpentine, and is never so agreeable as that communicated by the fresh peel of the fruit, especially when removed by rubbing the lemon against a piece of loaf-sugar. The specific gravity of lemon oil is about 0.847 at  $70^{\circ}$ , and its boiling-point is about  $230^{\circ}$ , the density of its vapor being 4.77. (SOUBEIRAN and CAPITAINE; CAHOURS, *Ann. Ch. et Ph.*, LXX. 103.) It is therefore isomeric with turpentine oil. It does not solidify when cooled down to  $4^{\circ}$ . It dissolves readily in absolute alcohol and in ether; but spirit of wine, of sp. gr. 0.825, only dissolves about 14 per cent. of it.

When oil of lemon is long exposed to the air, it absorbs oxygen, and there then frequently forms in it a white brittle crystalline substance, having the odor of the oil, fusible at  $115^{\circ}$ , and subliming at a higher temperature without decomposition: it consists, according to Mulder, of  $C_{10}H_5O_5$ , its formation being apparently attended by the production of water. ( $C_{10}H_8 + O_8 = C_{10}H_5O_5 + 3HO$ .) By the



joint action of alcohol and nitric acid, a crystalline *hydrate of citrene* is obtained, closely resembling, and isomeric with, the corresponding terpentine or camphene compound, its formula being  $C_{10}H_8 + 3HO = C_{10}H_9O + 2HO$ ; by sublimation it loses 1 atom of water, and becomes  $C_{10}H_9O + HO$ .

*Hydrochlorate of Oil of Lemons.*  $C_{10}H_8 + HCl = C_{10}H_9Cl$ . *Artificial Lemon-Camphor.* This substance (*Mém. d'Arcueil*, ii. 32) is produced by passing hydrochloric acid gas into essence of lemons, which absorbs it in large quantity; and yields a considerable crystalline deposit, especially if the oil is well rectified and artificially cooled, and the acid gas previously dried. The crops of crystals must be pressed between folds of filtering paper, so as to free them from mother-liquor, and purified by solution in and crystallization from hot alcohol; they are then white, of an agreeable odor, and admit of sublimation when gently heated, without suffering any decomposition.

When this compound is acted upon by potassium, it yields a compound resembling that from terpentine-camphor; and another similar oil is obtained by distilling the brown mother-liquor of the crystalline combination, off quicklime. These isomeric oils have been termed *citrene* and *citrilene*. (DUMAS, *Ann. Ch. et Ph.*, lii. 49 and 405. BLANCHET and SELL, *Ann. der Pharm.*, vi. 284.)

OIL OF ORANGE PEEL closely resembles the preceding; it forms similar compounds with chlorine and hydrochloric acid. (SOUBEIRAN and CAPITAINÉ.) Its sp. gr. is 0·835; it boils at about 355°; it possesses a remarkable power of rotating a polarized ray to the *right*.

OIL OF BERGAMOT. According to Dumas, and to Soubeiran and Capitaine, (*Journ. de Pharm.*, xxvi. 68,) this oil, which is obtained from the ripe fruit of *Citrus bergamium*, is of the same composition as oil of lemons; but when it is submitted to distillation, the first portion which passes over has the sp. gr. of 0·850, while the last portion has sp. gr. 0·877. It appears probable that the last portion is an oil containing oxygen, and Ohme (*Ann. der Pharm.*, xxxi. 316) assigns to the original oil the formula  $C_{30}H_{26}O_2$ ; but this may also be represented as  $3 [C_{10}H_8] + 2HO$ . According to Deville, when oil of bergamot is treated with alcohol and nitric acid, it yields a *crystalline hydrate*, having all the properties of the corresponding product from oil of lemon. There are so many contradictory statements respecting the composition and properties of this oil, as to show that it requires additional examination.

OIL OF ORANGE FLOWERS. *Oleum neroli*. According to Henry and Plisson, (*Journ. de Pharm.*, xvii. 450,) this oil contains rather more than 1 per cent. of oxygen; this is, however, probably accidental only, and in its pure state it may be regarded as belonging to the *hydrocarbons*. It is obtained by distilling fresh orange-flowers with water, and is first pale-yellow, but becomes much deeper-colored under the influence of light. It has an agreeable, though somewhat mawkish odor, of the flower. According to Soubeiran, it includes two distinct oils, one of which is much more soluble in water than the other, and is that principally concerned in the flavor of *orange-flower water*. Plisson also obtained a crystallizable substance from this oil.



OIL OF JUNIPER is obtained by distilling juniper berries with water; the full-grown green berries yielding a larger produce than the ripe fruit, in consequence of a portion of the oil having, in the latter, passed into resin. According to Blanchet, juniper oil is separable into two distinct oils as to density; the one having a sp. gr. of 0·855; the other of 0·881; but they are both =  $C_{10}H_8$ . Soubeiran and Capitaine found the density of the vapor of the oil to be 4·8, so that it may be considered isomeric with oil of turpentine.

OIL OF SABINE, from *Juniperus Sabina*; OIL OF PARSLEY, from *Apium petroselinum*; OIL OF PEPPER, the volatile oil of *Piper nigrum*; and OIL OF CUBEBS, from the fruit of *Piper cubeba*, are among the principal essential oils which contain no oxygen, and are isomeric with turpentine and lemon oil.

OIL OF LAUREL. *Laurel turpentine*. (STENHOUSE. *Mem. Chem. Soc.*, i. 45.) An essential oil, under these names, is imported from Demerara, and other parts of South America; its source has not been well ascertained, but it is probably derived from a species of pine. Its odor partakes both of lemon and of turpentine: its sp. gr. is 0·864. It appears to consist of two isomeric oils, belonging to the tribe of hydrocarbons of which turpentine oil is the type.

OIL OF ELEMI. When the resinous substance, known under the name of *gum elemi*, and which is said to be the produce of the *Amyris Elemifera*, but which is probably obtained from other terebinthaceous trees, is submitted to distillation with water, a small quantity of volatile oil passes over, which, according to Stenhouse and Deville, has the same composition as oil of turpentine, and produces two hydrochlorates.

OIL OF STYRAX. *Styrole*. By distilling *liquid storax*, or “balsam of storax,” Simon (*Ann. der Pharm.*, xxxi. 265) obtained an oil, which was found by Marchand to consist of 2 atoms of carbon with 1 of hydrogen. Blythe and Hofmann examined this product in 1844, (*Mem. Chem. Soc.*, ii. 334,) and confirmed the results obtained by Marchand; they also ascertained a very remarkable character belonging to Styrole, namely its conversion by heat into *Metastyrole*, a soft viscid solid, perfectly transparent, and having the same high refractive power as the original styrole. This curious change they first felt inclined to attribute to the absorption of oxygen, but they found it take place in sealed tubes, and demonstrated the perfect isomerism of the two different forms of this curious substance, the further properties and combinations of which are fully described in the memoir which I have quoted. According to Blythe and Hofmann, styrole is in the highest degree volatile, evaporating at common temperatures so rapidly that oily spots made by it on paper disappear in a few seconds. Its sp. gr. is 0·924; it boils at about 295°. They assign to it the formula  $C_{16}H_8$ . (See *Balsams*.)

By distilling *tolu balsam*, Deville obtained, amongst other products, (*Ann. Ch. et Ph.*, 3ème Sér., iii. 168) an oily body which has been subsequently examined by Muspratt and Hofmann (*Mem. Chem. Soc.*, ii. 367,) and to which they have given the name of *Toluole*: its formula is  $C_{14}H_8$ . (See *Balsams*.)



The hydrocarbon obtained by Gerhardt and Cahours, by distilling cinnamic acid with excess of baryta, (see page 1490,) and since examined by Kopp (*Comptes Rendus*, xxi. 1376) appears to be identical with styrole, having the formula  $C_{16}H_8$ .

## II. ESSENTIAL OILS CONSISTING OF CARBON, HYDROGEN, AND OXYGEN.

The greater number of essential oils belong to this class; and although, as already stated, many of them admit of resolution into two oils, of which one is a hydrocarbon, and the other an oxyhydrocarbon, and others may be rationally represented as hydrates of hydrocarbons, yet, there are also many to which no such formulæ can be properly assigned. Some of these oils are extremely interesting, as having been formed artificially, and also in consequence of their connection with, or relations to, other organic products; as in respect to the oil of bitter almonds, the oil of spiræa, and the oil of cinnamon, which have already been described. The following are the principal of these oils which have been minutely examined, and which are not noticed elsewhere, under other heads.

**OIL OF CLOVES.** The *clove* of commerce is the unexpanded flower of the *Caryophyllus aromaticus*, a tree cultivated in the Molucca Islands, as well as at Sumatra, Mauritius, Bourbon, Martinique, &c. The corolla forms a small globe at the top, between the four teeth of the calyx, and thus, with the tapering and angular tube of the calyx, gives the nail-like character to the *clove* (from the French *clou*, a nail.) The cloves from the East Indies, under the name of *Amboyna* and *Bencoolen cloves*, are the plumpest and most esteemed; those produced in the French possessions (*Bourbon* and *Cayenne cloves*) are shrivelled, less oily, and of very inferior value.

To extract the whole of the oil from cloves, they require to be subjected to repeated distillations, for it is one of the least volatile of these oils. When freshly distilled it is of a pale yellow color, but it becomes brown by keeping, and its alcoholic solution, which is at first colorless, gradually deepens in tint. Its sp. gr. varies between 1.05 and 1.06. It is composed of two distinct oils, one of which is *indifferent*, incapable of combining with bases, and has a sp. gr. of 0.918; the other possesses *acid* characters, and its sp. gr. is 1.079. The indifferent oil is a hydrocarbon of the class  $C_{10}H_8$ . The acid oil, which has been termed *Eugenic acid*, has the formula  $C_{24}H_{15}O_5$ . (ETTLING and BÖCKMANN, *Poggend. Ann.*, xxxi. 526. *Ann. der Pharm.*, xxvii. 155.)

*Eugenic Acid* is obtained by adding a concentrated solution of potassa to oil of cloves, with which it forms a buttery crystalline mass; this is mixed with water, and distilled, till oil no longer passes over; dilute sulphuric acid is then added to the residue in the retort, and the distillation resumed, when eugenic acid passes over. Eugenic acid may be obtained by similarly treating the *oil of pimenta* (the fruit of *Myrtus pimenta*), and is also contained, according to Meyer and Reiche (*Ann. der Pharm.*, xlvii. 234,) in the essential oil of *Canella alba*.

Eugenic acid is a transparent, colorless, oily liquid, sp. gr. 1.079; it has a strong odor of cloves, and a burning aromatic flavor; it is very sparingly soluble in water, but abundantly so in alcohol, ether, acetic

acid, and fat oils. It reddens litmus. Its boiling-point is above  $470^{\circ}$ ; it does not concrete at  $0^{\circ}$ ; exposed to the air it becomes brown, in consequence of the absorption of oxygen; and when it is, in this state, distilled, it leaves a brown resinous residue: it is reddened by nitric acid, and when heated, considerable action ensues, and oxalic acid is formed. It absorbs chlorine with the production of hydrochloric acid, and a resinoid compound is the result. It is decomposed and partly converted into a resinous substance, by sulphuric acid. It consists of

|                    |    |     |     |     |        | Ettling. | Bückmann. | Liebig. |         |     |        |
|--------------------|----|-----|-----|-----|--------|----------|-----------|---------|---------|-----|--------|
| Carbon .....       | 24 | ... | 144 | ... | 72·36  | ...      | 72·633    | ...     | 72·696  | ... | 73·12  |
| Hydrogen .....     | 15 | ... | 15  | ... | 7·54   | ...      | 7·437     | ...     | 7·434   | ... | 7·23   |
| Oxygen .....       | 5  | ... | 40  | ... | 20·10  | ...      | 19·930    | ...     | 19·870  | ... | 19·65  |
| <hr/>              |    |     |     |     |        |          |           |         |         |     |        |
| Eugenic acid ..... | 1  |     | 199 |     | 100·00 |          | 100·000   |         | 100·000 |     | 100·00 |

The *eugenates* have been principally examined by Bonastre, (*Ann. Ch. et Ph.*, xxxv. 274); they have the taste and smell of the acid, and are reddened by nitric acid, and rendered purple, and brown, by persalts of iron.

*Eugenate of Ammonia.* Eugenic acid absorbs ammonia, and produces a granular buttery compound, which when warmed, loses ammonia, and leaves a salt composed of  $\text{NH}_3$ ,  $2[\text{C}_{24}\text{H}_{15}\text{O}_5]$ . (ETTTLING.)

*Eugenate of Potassa* forms silky crystals, composed, according to Dumas, of  $\text{KO}$ ,  $2[\text{C}_{24}\text{H}_{15}\text{O}_5] + \text{HO}$ ; or, when dried at  $212^{\circ}$ , their composition, deduced from the analysis of Bonastre and Ettling, may be represented by  $2\text{KO}$ ,  $3[\text{C}_{24}\text{H}_{15}\text{O}_5]$ .

*Eugenate of Soda* forms bundles of silky acicular crystals.

*Eugenate of Baryta*, formed by agitating the acid with baryta water, dissolving the product in boiling water, and crystallizing, forms white pearly scales. There appear to be two eugenates of baryta, one of which contains 17 and the other 32 *per cent.* of baryta.

*Eugenate of Strontia* crystallizes in white needles.

*Eugenate of Lime* is not crystallizable, and is very little soluble in water.

*Eugenate of Lead.* When a solution of eugenate of potassa is mixed with basic acetate of lead, a dense yellow precipitate falls, which softens when boiled in the liquor. Ettling represents it as  $3\text{PbO}$ ,  $\text{C}_{24}\text{H}_{15}\text{O}_5$ , and found in it 62.6 *per cent.* of oxide of lead. According to Dumas, who assigns to eugenic acid the formula  $\text{C}_{20}\text{H}_{12}\text{O}_4$ , the basic eugenate contains only 49.2 *per cent.* of oxide of lead: so that there is probably more than one combination.

*Eugenate of Iron.* A hot solution of eugenate of potassa produces a precipitate with protosulphate of iron, which is first white, but becomes presently blue. With sulphate of *copper* a brown compound is formed, which, when boiled for some time in the liquor, becomes blue or green.

*Eugenie. Clove-oil Camphor.* This substance is deposited in small crystals by water which has been distilled from cloves, (the *clove-water* of pharmacy.) It acquires a yellow color by exposure to air. According to Dumas, it is isomeric with eugenic acid. The formulæ  $\text{C}_{24}\text{H}_{15}\text{O}_5$ , and  $\text{C}_{20}\text{H}_{12}\text{O}_4$ , have each been assigned to it.

*Caryophylline.* This substance, which has also been termed *clove-*



*camphor*, is deposited in a crystalline form by a strong alcoholic tincture of cloves. It may also be obtained by distilling the greater part of the alcohol from the tincture, and adding water to the residue, when the caryophylline is precipitated, and may be purified by solution in, and crystallization from alcohol. It forms spherical aggregates of acicular crystals, inodorous, insipid, insoluble in water, sparingly soluble in alcohol, and very soluble in ether. At about  $540^{\circ}$  it rises in vapor, but does not fuse, even at a higher temperature. In composition it appears to be isomeric with common camphor, namely,  $C_{10}H_{16}O$ . (DUMAS. MYLIUS. *Erdmann and Marchand's Journ.*, xxii. 105.)

**OIL OF CUMIN.** This oil, which is the produce of the seed of the *Officinal Cumin* (*Cuminum cyminum*), a plant extensively grown in Malta and Sicily, has been specially examined by Gerhardt and Cahours. (*Ann. Ch. et Ph.*, 3ème Sér., i. 60.) It has a strong disagreeable odor, and a pungent acrid flavor; it is of a yellowish color, especially after having been exposed to air, which gives rise to the formation of a resinous, as well as of an acid product, so that under these circumstances, the oil reddens litmus. The boiling-point of cumin oil is far from constant; it begins to boil at  $340^{\circ}$ , but the thermometer soon mounts to  $445^{\circ}$ , and the oil which last passes over, is most oxygenized; it is evidently therefore a mixture of oils of different volatility. By the action of caustic potassa, Gerhardt and Cahours succeeded in separating these components of the crude oil of cumin; thus, by rectifying the portion of the oil which first distils, over caustic potassa, they procured a *hydrocarbon* =  $C_{20}H_{14}$ , which they designate *Cymene*. The less volatile portion of cumin oil is an *oxyhydrocarbon*, and they distinguish it by the term *Cuminole*, its formula being  $C_{20}H_{12}O_2$ .

*Cymene* is a powerfully refracting colorless liquid, of an agreeable lemon odor; its boiling-point is  $330^{\circ}$ , and it distils over without change: it is not acted on by air, is insoluble in water, but soluble in alcohol, ether, and essential oils. The density of its vapor is 4.69. It combines with the fuming sulphuric acid to produce *sulphocymenic acid*, the formula of which is  $C_{20}H_{13}S_2O_5$ , or  $C_{20}H_{13}\begin{cases} S \\ O_2 \end{cases}SO_3$ . The *sulphocymenates* have been examined by Gerhardt and Cahours, in the memoir quoted, and also by Delalande. (*Ann. der Pharm.*, xxxviii. 342.)

*Cuminole* is obtained by distilling the crude oil of cumin in an oil-bath heated to  $392^{\circ}$ . As cymene boils at  $330^{\circ}$ , the whole of it passes over into the receiver, carrying a considerable portion of cuminole with it; but, if the distillation of the original oil be carefully conducted at the above-mentioned temperature, what remains in the retort is cuminole. It may be distilled over at a higher temperature, but the process must be rapidly conducted in a current of carbonic acid, and the product preserved in a well-stopped phial; the facility with which cuminole is changed by oxygen, rendering these precautions necessary.

Cuminole is colorless, or slightly yellow; it has a strong persistent odor of cumin, and a hot pungent taste; its boiling-point is  $430^{\circ}$ . When heated in the contact of air, it acquires color and acidity, and a portion of it is resinified. The acid thus produced, *cuminic acid*, may be speedily obtained by the action of bichromate of potassa and sulphuric



acid, upon cuminole; or by dropping into it fused caustic potassa; in the latter case hydrogen is evolved, and *cuminate of potassa* immediately formed.

*Cuminic Acid*,  $C_{20}H_{11}O_3 + H_2O$ , is best obtained by fusing potassa in a retort, into the tubulature of which a small drawn-out tube has been inserted so as to admit of oil of cumin being gradually dropped into it; cuminate of potassa is immediately formed, and the *cymene* of the oil distils over. If the latter is not preserved, the process may be simplified by performing it in an open capsule. The resulting cuminate is then dissolved in water, and decomposed by nitric acid, which should be added in slight excess; it precipitates the whole of the cuminic acid in the form of white or yellowish flocks, which must be washed upon a filter, and then carefully fused; on cooling, it concretes, and the adhering water separates from it, and may easily be removed. If it contain any resin, it may be purified by sublimation, and crystallization from solution in alcohol.

Thus prepared, cuminic acid forms perfectly white prismatic tables, of an acid taste, and a slight odor resembling that of bugs. It fuses at  $196^\circ$ , floating upon boiling water in the form of a colorless oil, which concretes on cooling; its boiling-point is about  $480^\circ$ , but it sublimes at a much lower temperature when boiled with water; the density of its vapor, which is acid, and suffocating, is 5.7; it may be condensed in beautiful needles. This acid is almost insoluble in cold water, and the small portion taken up by boiling water falls on cooling. It is more soluble in acidulated water, so that in precipitating it, great excess of nitric acid should be avoided. It is readily soluble in alcohol and in ether, which leave it crystallized, on evaporation. When pure it is not discolored by, but dissolves in sulphuric acid. Boiled with nitric acid it forms *nitro-cuminic acid*, in which, an atom of its constituent hydrogen is replaced by  $NO_4$ . Subjected to dry distillation with excess of caustic baryta, it is decomposed into carbonic acid, which remains united to the base, and into *cumène*, a fragrant colorless liquid hydrocarbon, having the formula  $C_{18}H_{12}$ , and combining with fuming sulphuric acid to form *sulphocuménic acid*  $= C_{18}H_{12}, S_2O_5$ . The action of chlorine, bromine, and potassium, on cuminole, are also described by Gerhardt and Cahours.

The formula of the *anhydrous cuminic acid* (in combination with bases) is  $C_{20}H_{11}O_3$ . The elements of the *crystallized cuminic acid*, are the same as those of the *sublimed acid*, namely,  $C_{20}H_{11}O_3 + H_2O$ , or

|                                |    |      |     |      |        | Gerhardt<br>and Cahours. |
|--------------------------------|----|------|-----|------|--------|--------------------------|
| Carbon .....                   | 20 | .... | 120 | .... | 73.17  | .... 73.15               |
| Hydrogen .....                 | 12 | .... | 12  | .... | 7.32   | .... 7.52                |
| Oxygen .....                   | 4  | .... | 32  | .... | 19.51  | .... 19.33               |
| <hr/>                          |    |      |     |      |        | <hr/>                    |
| Crystallized cuminic acid..... | 1  |      | 164 |      | 100.00 | 100.00                   |

*Cuminates.* Cuminic acid expels carbonic acid from the carbonates; it forms well-defined salts, which may be obtained, both directly, and by double decomposition; several of them have been examined and analyzed by Gerhardt and Cahours. (*Ann. Ch. et Ph.*, 3ème Sér., i. 74.)

*Cuminate of Ammonia*,  $NH_4O, C_{20}H_{11}O_3$ , obtained by saturating caustic ammonia with cuminic acid, forms tufts of slender crystals, which



effloresce in the air, and probably lose ammonia and pass into an acid salt. A weak solution of this cuminate produces no precipitate in lime or baryta water, nor in moderately strong solutions of chloride of calcium, or chloride of barium: it gives a buff-colored precipitate with the persalts of iron, and a pale blue with the salts of copper.

*Cuminate of Potassa* is deliquescent, and not regularly crystallizable.

*Cuminate of Baryta*,  $\text{BaO}$ ,  $\text{C}_{20}\text{H}_{11}\text{O}_3$ , is obtained in white nacreous crystals, by the action of a solution of cuminic acid upon carbonate of baryta; if a hot concentrated solution of the acid be used, the salt precipitates immediately as the liquor traverses the filter, and each crystal, at the moment of its formation, reflects light in brilliant iridescent colors. This salt is very bitter, and soluble in alcohol and in ether.

*Cuminate of Silver*,  $\text{AgO}$ ,  $\text{C}_{20}\text{H}_{11}\text{O}_3$ , is thrown down in the form of a white curdy precipitate, which speedily blackens in the light, when cuminate of ammonia is added to nitrate of silver: when this salt is subjected to dry distillation, it leaves a carburet of silver,  $= \text{AgC}$ , which is of a dull yellow color, and resists the action of heat.

**OIL OF ANISE.** This is the essential oil of the seed of *Pimpinella anisum*, a plant largely cultivated in Spain, Malta, and several parts of Germany. Oil of anise is imported chiefly from Germany, and sometimes from the East Indies. It has a pale yellow color, and a strong persistent odor of the seed; it usually congeals at about  $50^\circ$ , and remains solid up to between  $60^\circ$  and  $70^\circ$ . By exposure to air it acquires viscosity, and its tendency to solidification diminishes. The *Oleum Badiani*, or oil of star-anise (*Illicium anisatum*) a plant belonging to the *Winteraceæ*, growing in Japan and Cochin-China, is said sometimes to be substituted for the common anise oil, and to congeal less readily. The elaioptene of anise oil seems not to have been much noticed, but the stearoptene, or concrete portion (*anise-camphor*), has been examined by Dumas (*Ann. Ch. et Ph.*, L. 225,) and made the subject of a more elaborate inquiry by Cahours. (*Ann. Ch. et Ph.*, 3ème Sér., ii. 274.) He obtained it by pressing the common concrete anise oil of commerce between folds of blotting-paper, as long as it soiled the paper; it was then dissolved in alcohol and crystallized two or three times from that solvent: it was then perfectly white, very nearly of the same specific gravity as water, of a weaker, but more agreeable odor of anise, than the crude oil, and very friable, especially at  $32^\circ$ . It fuses at about  $65^\circ$ , and boils at  $430^\circ$ , volatilizing with very little alteration. Air does not affect it whilst concrete, but in its fluid state it gradually changes it into resin. The analysis of concrete anise-oil shows that it is isomeric with cuminole, being  $\text{C}_{20}\text{H}_{12}\text{O}_2$ ; and both are derived from umbelliferous plants; but different re-agents produce very different effects upon these two oils.

One of the most definite compounds of anise oil is that which it forms with bromine, called by Cahours *Bromanisal*,  $= \text{C}_{20}\text{H}_9\text{O}_2\text{Br}_3$ : they act upon each other with the evolution of heat and of hydrobromic acid, and form a solid compound, which, purified by crystallization from its solution in ether, is inodorous, insoluble in water, but little soluble in alcohol, and much more soluble in ether. It is decomposed at a temperature a little above  $212^\circ$ . The action of *chlorine* on concrete anise oil is much less definite, and the resulting products are viscid, semi-fluid

compounds. By the action of concentrated sulphuric acid on the concrete oil, a resinous substance is produced, termed by Cahours *Anisoïne*; it is white, inodorous, fusible at a little above  $212^{\circ}$ , insoluble in water, scarcely soluble in alcohol, but more so in ether and in volatile oils; it is deposited from its ethereal solution in minute acicular crystals. The same substance appears to be produced by other strong acids, and especially by the phosphoric, and by certain anhydrous chlorides. The analysis of anisoïne leads to the inference that it is perfectly isomeric with the original concrete essence, its formula being  $C_{20}H_{12}O_2$ .

*Anisic Acid.*  $C_{16}H_6O_5 + HO$ . Under this name Cahours describes a crystalline product formed, along with a yellow resinoid, by the action of diluted nitric acid upon anise oil; it is purified by washing it in the first instance with water, then dissolving it in ammonia, and recrystallizing the ammoniacal salt till colorless. This *anisate of ammonia* may then be decomposed by acetate of lead, which throws down an *anisate of lead*; and this, decomposed by sulphuretted hydrogen, yields a solution, from which anisic acid is obtained on evaporation, and which may be finally purified by sublimation.

Anisic acid forms colorless acicular crystals, almost insoluble in cold water, but considerably soluble in boiling water, which on cooling deposits it in crystals. It is very soluble in alcohol and in ether, and forms soluble crystallizable salts with the alkalis and earths. The *anisates of lead*, and of *silver*, are, to a certain extent, soluble in boiling water, which, on cooling, deposits them in small crystals. *Anisic acid* resembles benzoic, and cinnamic acid, in being volatile without decomposition, and in precipitating the salts of peroxide of iron, but not those of the protoxide. The formula of *anisate of silver* dried *in vacuo*, at  $250^{\circ}$ , is  $AgO, C_{16}H_6O_5$ ; that of *anisate of lead*, similarly dried, is  $PbO, C_{16}H_7O_6$ ; so that the latter obstinately retains an atom of water. (CAHOURS.)

When crystallized anisic acid is distilled with excess of baryta it yields *anisoïe*, a colorless and very mobile liquid, of an agreeable aromatic odor, boiling at about  $302^{\circ}$ . It is insoluble in water, but soluble in alcohol and in ether. It forms crystallizable volatile compounds with chlorine and bromine, and produces a coupled acid when acted upon by fuming sulphuric acid. Its formula is  $C_{14}H_7O_2$ .

When oil of anise is boiled with nitric acid of sp. gr. 1.3, till the whole of the products which it forms are dissolved, the liquor deposits, on dilution, a yellow flocculent matter, which is impure *nitroanisic acid*. To purify it, it is well washed, and dissolved in ammonia; the *nitroanisate of ammonia* thus formed, is crystallized till colorless, and decomposed by an acid; the precipitate which falls is then well washed with distilled water. Thus prepared, nitroanisic acid is a pale yellow substance, very little soluble either in cold or hot water; it is deposited in small needles by its hot saturated aqueous solution. It is also soluble in hot alcohol. When carefully heated it is partly volatilized and partly decomposed. The *nitroanisates of ammonia*, *potassa*, and *soda*, are very soluble; with *lime*, *baryta*, *strontia*, and *magnesia*, the salts are sparingly soluble, and with *lead* and *silver*, insoluble. The formula of *anhydrous nitroanisic acid*, as it exists in the silver salt dried at  $260^{\circ}$  *in vacuo*, is  $C_{16}H_5O_9N$ . *Crystallized nitroanisic acid* is  $C_{16}H_5O_9N + HO$ .

When concrete oil of anise is acted upon by fuming nitric acid, a



yellow resin-like substance is formed, called by Cahours *Nitraniside*, and to which he assigns the formula  $C_{20}H_{10}O_{10}N_2$ .

**OIL OF WILD FENNEL.** (*Fœniculum vulgare*, or *Bitter Fennel*.) This oil has also been examined by Cahours; it is limpid and pale yellow at ordinary temperatures; it congeals by cold, though less readily than anise oil. It consists of a volatile hydrocarbon, having the formula  $C_{10}H_8$ , and an oxyhydrocarbon, of the same composition as concrete anise oil. By passing binoxide of nitrogen into the more volatile portion of this oil, Cahours obtained a white crystalline compound  $= C_{15}H_{12}O_4N_2$ ; this substance therefore is a combination of nitric oxide with a hydrocarbon isomeric with turpentine and lemon oil.

**PEPPERMINT OIL**, obtained by distilling the herb (*Mentha piperita*) with water, has a very pale yellow or greenish-yellow tint, which somewhat deepens by age. It has a strong odor of the plant, and a hot, aromatic flavor, succeeded by a sense of coldness upon the tongue. The products of the distillation of peppermint oil at different temperatures have not been minutely examined; but the last portions which pass over when it is rectified, deposit, when duly cooled, a concrete substance. The American oil of peppermint, which is said to be prepared from the dried plant gathered when in flower, yields a considerable portion of this stearoptene when cooled down to  $32^\circ$ , and it admits of being easily removed, and pressed between folds of paper, so as to free it from the liquid oil. This crystallized product, called *peppermint-camphor*, has been examined by Blanchet and Sell, (*Journ. de Pharm.*, xx. 345,) by Dumas, (*Ann. Ch. et Ph.*, L. 225,) and by Walter (*ibid.* Lxxii. 83): their analyses represent it by the formula  $C_{10}H_{10}O, = C_{10}H_9 + HO$ . It forms colorless prismatic crystals having the odor and taste of peppermint, almost insoluble in water, but abundantly soluble in alcohol, and ether, and in sulphuret of carbon, but less soluble in oil of turpentine; it fuses at about  $92^\circ$ , and boils at  $415^\circ$ , the density of its vapor being 5.45. If the equivalent of this substance be regarded as representing 4 volumes of its vapor, its formula will be  $C_{20}H_{20}O_2$ .

By distilling peppermint-camphor with anhydrous phosphoric acid, Walter obtained a liquid hydrocarbon, the density of the vapor of which is 4.835: this liquid has been termed *Menthène*, and assuming one equivalent of it to represent 4 volumes of its vapor, the formula of menthène will be  $C_{20}H_{18}$ . If therefore the original camphor be represented as  $C_{20}H_{18} + 2HO$ , (the formula assigned to it by Walter), then the action of the phosphoric acid has deprived it of 2 atoms of water, in converting it into menthène. Distilled with perchloride of phosphorus, peppermint-camphor yields *Chloromenthène*  $= C_{20}\frac{H_{17}}{Cl}$ ; and under the influence of a continuous current of chlorine, a liquid product is obtained,  $= C_{20}H_{13}Cl_5$ , in which therefore 5 equivalents of hydrogen are replaced by 5 of chlorine. It does not form a coupled acid with sulphuric acid.

**OIL OF CEDAR-WOOD**, originally described by Bonastre, (*Journ. de Pharm.*, xxiii. 177,) has been also examined by Walter, (*Ann. Ch. et Ph.*, 3ème Sér., i. 498); it is obtained from the cedar-wood of Virginia, in the



form of a soft white crystalline mass, which, after having been deprived of water by heat, solidifies at about  $80^{\circ}$ . Distilled in an oil-bath at a temperature between  $525^{\circ}$  and  $575^{\circ}$ , the greater part passes over at about  $540^{\circ}$ , and separates into a crystalline and a liquid portion. The solid portion, purified by pressure, and by solution in, and crystallization from alcohol, has an agreeable odor, resembling that of the wood; it fuses at  $165^{\circ}$ , and boils at  $540^{\circ}$ . It is very slightly soluble in water, but abundantly in alcohol, from which it separates in brilliant silky crystals. The density of its vapor is 8.15. It may be represented as composed of  $C_{32}H_{26}O_2$ ; or by the rational formula,  $C_{32}H_{24} + 2HO$ . When distilled with anhydrous phosphoric acid, the concrete cedar-oil yields *cedréne*, which is a slightly yellow liquid  $= C_{32}H_{24}$ ; it has a peculiar aromatic odor, perfectly distinct from that of the crystallized product, or *cedar-camphor*, and a taste at first slight, but afterwards peppery and persistent; it boils at about  $480^{\circ}$ , and the density of its vapor (calculated) is 7.5. The action of sulphuric acid, and of perchloride of phosphorus upon *cedréne* is the same as upon *menthène*.

**OIL OF ROSES.** This oil, under the name of *attar* or *otto of roses*, is extensively prepared in the East, especially at Ghazeepoor in Hindostan, and at Shiraz in Persia; it is probably all obtained by distillation; but, according to some authorities, it may be also procured by macerating the petals in water. This produce of the rose appears to be greatly modified by climate, for in distilling rose-water in this country, the oil which goes over is a concrete fatty matter, having somewhat of the odor of the rose, but entirely deficient in the persistent fragrantcy of the foreign perfume. Even in the East, the produce of attar from a given quantity of flowers, seems to be small; according to Polier (*Asiatic Researches*, i. 332,) 100 pounds of roses yield about 3 drachms. Heber says, that 20,000 roses produce attar equal in weight to that of a rupee. (*Narrative*, i. 266.) It is usually imported from Smyrna and Constantinople, in ornamental bottles of various shapes and sizes. It is of a pale yellow tint, and when it has been solidified by cooling, it requires a temperature of about  $80^{\circ}$  for its liquifaction, so that it generally is partly concrete, and often contains fine crystalline flakes of stearoptene, or *rose-oil camphor*. Its odor is extremely strong, but when properly diluted, as by solution in alcohol (*esprit de rose*), it is very agreeable, and much resembles that of the fresh flower.

Rose oil has been examined by Saussure, (*Journ. de Pharm.*, 1820,) by Blanchet, (*Ann. der Pharm.*, vii. 154,) and by Göbel, (*Kästner's Archiv.*, xvi. 297.) At  $57^{\circ}$ , 1000 parts of alcohol, sp. gr. 806, dissolve 7.5, and at  $72^{\circ}$ , 33 parts of this oil. When the concrete oil is agitated with alcohol, the adhering liquid oil is removed, and the stearoptene remains in the form of a white crystalline substance; it has comparatively little odor, and when pure is said to be inodorous; after fusion it concretes at about  $95^{\circ}$ . Its boiling-point is about  $540^{\circ}$ . It is copiously soluble in ether. It appears, from the analysis of Blanchet, to be one of the isomeric varieties of  $C_{12}H_{16}$ , the formula assigned to it being  $C_{16}H_{16}$ . Herberger has examined the fatty matter which collects, as above stated, upon the surface of rose-water; it is readily fusible, and volatile without decomposition; it dissolves in 480 parts of alcohol, and also dissolves in



ether and essential oils. By the protracted action of nitric acid, it yields oxalic acid. It is not affected by potassium. (*Buchner's Repertorium*, lxxviii. 101.)

OIL OF RUE, obtained by distilling the herb (*Ruta graveolens*) with water, is of a greenish-yellow color, has the peculiar disagreeable odor of the plant, and an aromatic, bitter, and hot taste. Its boiling-point is very high. When first distilled, it is colorless. The formula assigned to it is  $C_{28}H_{28}O_3$ , and the density of its vapor is 7.7. (WILL, *Ann. der Pharm.*, xxxv. 235.)

LAVENDER OIL. The true oil of lavender is obtained by distilling the flowers of garden lavender, *Lavandula vera*, with water; the English oil, which is most esteemed on account of its fragraney, is chiefly prepared at Mitcham in Surrey, where the plant is extensively cultivated for the purpose; it is an important article of perfumery, and is in highest perfection when about a year old. It is at first nearly colorless, but gradually acquires a pale amber tint. This oil is also a mixture of an elaioptene and stearoptene, but as their point of vaporisation is very nearly the same, they are difficultly separated. According to Dumas, the stearoptene, or lavender-camphor, of the oil grown in the south of Europe, amounts sometimes to half its weight. This oil appears to be an oxide of an hydrocarbon isomeric with that of turpentine oil; it has been represented by the formula  $C_{15}H_{14}O_2 = 3[C_5H_4] + 2HO$ .

An inferior oil is obtained from the *Lavandula spica* or *latifolia*, and is generally known in commerce under the name of oil of spike; it is sometimes used in varnishes, and as a vehicle for colors, and is principally imported from the south of Europe.

OIL OF ROSEMARY, from *Rosmarinus officinalis*, has the strong aromatic odor of the plant; it is a mixture of a hydrocarbon  $= C_{10}H_8$ , and a stearoptene; the latter is sometimes deposited by this oil when it has been kept in imperfectly closed vessels. When rosemary oil is distilled, the boiling point gradually rises; the distillate has the sp. gr. 0.885 to 0.887, and is represented by Dumas, as  $C_{80}H_{64} + 2HO$ ; that is, as a hydrate of a hydrocarbon isomeric with that of turpentine oil.

OIL OF CARAWAY. This oil is obtained from the seed of *Carum carui*, the common caraway, a plant found in pastures over the whole of Europe, naturalized in England, and largely cultivated in Essex. By distillation with water, the seed yields about 5 per cent. of a fragrant aromatic essential oil, of a pale-brown tint, which deepens by age. This oil has been examined by Völckel (*Ann. der Pharm.*, xxxv. 308), and by Schweitzer (*Erdmann and Marchand's Journ.*, xxiv. 257, and *Pharm. Central Blatt*, 1841, p. 782.) It is a mixture of a hydrocarbon which has been termed *caruine*,  $= C_{10}H_8$ , and of an oxyhydrocarbon, which, distilled with phosphoric acid, yields *caruole* (or *caracole*), a thick oil  $= C_{26}H_{18}O_2$ . The properties and combinations of these oils are detailed by Schweitzer.

OIL OF VALERIAN. When the root of common valerian (*Valeriana officinalis*) is distilled with water, an oil passes over, having, in an emi-

ment degree, the peculiar characteristic odor of the root. This oil consists, according to Gerhardt and Calours, of a hydrocarbon =  $C_{10}H_8$ , and an oxygenated oil, convertible into *valeric* (or *valerianic*) *acid*. When valerian oil is treated with nitric acid, and then saturated by carbonate of potassa, and subjected to distillation, it yields camphor. The acidity of water distilled off valerian was first observed by Pentz, who attributed it to the presence of acetic acid. (*Brandes' Archiv.* xxviii. 337.) It was first recognized and described as a peculiar acid, by Trommsdorff. (*Ann. Ch. et Ph.*, liv. 208.) The history of this acid has lately assumed much interest from its having been detected in a variety of products, and more especially in consequence of its artificial formation. It appears from the researches of Dumas and of Moro, that it exists in *phocenic acid*, and in the berries and bark of *Viburnum opulus*. Meyer and Zenner found it in the root of *angelica*. (*Ann. der Pharm.*, lv. 317.) Dumas and Stass obtained it from the volatile oil of corn-spirit (hydrate of oxide of amyle) and showed that it bears the same relation to that compound, as acetic acid does to alcohol, or formic acid to wood-spirit; and that by the catalytic action of finely-divided platinum under the influence of air, amyle, =  $C_{10}H_{11}$ , passed into *valeryle*, =  $C_{10}H_9$ , which, by oxidizement, becomes valeric acid. The researches of Balard, and of Iljenko and Laskowski (*Ann. der Pharm.*, lv. 79), have shown the presence of valeryle in the products of the decomposition of caseine.

*Valeric Acid*,  $C_{10}H_9O_3 + H_2O$ , is obtained: 1. By distilling water off valerian root as long as it reddens litmus; the acid water is then saturated by magnesia, or by carbonate of potassa or soda, and evaporated to dryness in a water-bath: the saline residue thus obtained, is then mixed with a sufficient quantity of sulphuric acid diluted with half its weight of water, and distilled: the distillate separates into two layers, the uppermost of which is a saturated aqueous solution of valeric acid, and the lowermost, an oily hydrate of the acid: this oily hydrate is then separated and submitted to distillation; the first portion which distils is aqueous, but when the boiling-point attains  $346^\circ$ , the pure hydrated acid passes over, unmixed with water. 2. By boiling 50 parts of *angelica* root, with water in which between 3 and 4 parts of caustic potassa have been dissolved; the decoction is strained, concentrated by evaporation, supersaturated by sulphuric acid, and distilled. The distillate is saturated by potassa, evaporated, and decomposed by distillation with sulphuric acid: after some time, crystals of *angelicic acid* form in the distilled liquor, whilst the valeric acid remains fluid. 3. The bark of *Viburnum opulus* is distilled with sulphuric acid and water, the distillate saturated with a basis, evaporated, and the salt decomposed by sulphuric acid. 4. *Hydrate of oxide of amyle* (oil of potato spirit) is mixed in a flask with 10 parts of a mixture of equal weights of quicklime and caustic potassa; as soon as the immediate action, which is attended by increase of temperature, is over, the flask is carefully heated in a fusible metal or oil-bath, first to  $340^\circ$ , and then to  $445^\circ$ , when hydrogen is evolved, and *valerate of potassa* formed. As soon as the disengagement of hydrogen ceases, the flask is closed, and allowed to cool; water is then quickly poured upon the mass in the flask, taking care to prevent access of air; dilute sulphuric acid is then added, and the mixture submitted to distillation. The distillate is saturated by carbonate of potassa, and the





*Valerates.* These salts have a sweetish taste, and several of them may be obtained crystallized, while others are amorphous. They vary considerably as to solubility in water: most of them dissolve in alcohol. By the action of stronger acids, including acetic and succinic acid, the valeric acid is separated from their solutions in the state of *terhydrate*. We are principally indebted to Trommsdorff, L. Bonaparte, and Chevreul, for our information respecting these salts. In obtaining them, the former used the acid distilled from valerian root; the latter, that derived from fish oil. The valerates are anhydrous.

*Valerate of Ammonia* may be crystallized by evaporating its solution, adding ammonia to restore that which escapes, and then placing it under a bell glass including a basin filled with solution of ammonia; groups of acicular crystals gradually form, which lose ammonia on exposure to air: they are soluble in alcohol, and when heated, first fuse, and then evaporate. *Valerate of Potassa* is a deliquescent, uncrystallizable, and very soluble salt. *Valerate of Soda* is deliquescent, but may be obtained in cauliflower crystals. This salt fuses at  $285^{\circ}$ , without loss of acid, and on cooling, concretes into a white solid. *Valerate of Lime* forms small stellated groups of prismatic crystals, which effloresce in dry air, and are much more soluble in water than in alcohol. This salt may be dried at  $265^{\circ}$  without decomposition, but at  $285^{\circ}$  it begins to lose acid. *Valerate of Baryta* crystallizes in small transparent prisms, soluble in 2 parts of water at  $60^{\circ}$ , and in their own weight at  $70^{\circ}$ . *Valerate of Strontia* forms efflorescent tabular crystals, soluble in water and in alcohol, and efflorescent. *Valerate of Magnesia* crystallizes in bundles of transparent prisms, efflorescent, very soluble in water, but less so in alcohol. Their taste is remarkably sweet. *Valerate of Manganese* forms irregular prisms, of a greasy appearance, and easily soluble. *Valerate of Iron* has not been obtained. Moist hydrated peroxide of iron is taken up by the acid in very small quantity only. When metallic iron is digested in the acid, it becomes brown in a few hours, and after some weeks a dark-brown liquor is formed, but it contains very little iron. *Valerate of Zinc* forms delicate lamellar crystals, soluble in water and in alcohol, permanent in the air, and fusible without decomposition at  $285^{\circ}$ . *Valerate of Cadmium* produces silvery crystals resembling boracic acid, feeling greasy, and soluble in alcohol. *Valerate of Cobalt.* Carbonate of cobalt readily dissolves in valeric acid, forming a pink solution, from which purple prismatic crystals may be obtained, easily soluble in water and in alcohol, permanent in the air, and of a sweet and astringent taste. *Valerate of Nickel.* Carbonate of nickel readily dissolves in the warm oily acid, forming a thick green liquid, perfectly soluble in hot dilute alcohol, and which, on evaporation, leaves a green difficultly-soluble powder. *Valerate of Copper* may be obtained in green prismatic crystals, (which include water of crystallization,) by evaporating a solution of carbonate of copper in warm aqueous valeric acid; they are easily soluble in water and in alcohol. At  $268^{\circ}$  they only lose a part of their water, and at a higher temperature become basic, by loss of acid. *Valerate of Lead.* When excess of oxide of lead is digested in valeric acid, and the mass extracted by water, filtered, and evaporated *in vacuo*, globular deposits of acicular crystals are obtained, very sparingly soluble in water, and which absorb carbonic acid: they are a *tribasic valerate*. When the oxide is



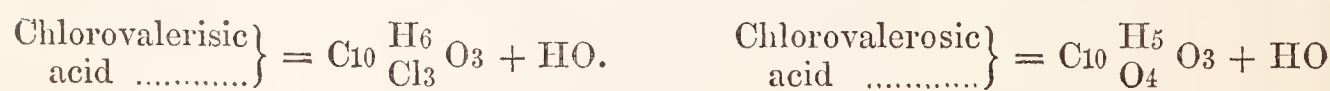
dissolved in the acid, and the solution evaporated, it yields lamellar crystals, very soluble and deliquescent, of the *monobasic* salt. *Valerate of Mercury* is formed by dissolving the red oxide in warm valeric acid; on cooling, the solution concretes into a buttery mass, which, dissolved in water, yields stellated groups of white acicular crystals. This salt is also obtained by the mutual decomposition of a solution of corrosive sublimate and valerate of potassa. When heated, the crystals lose water, and at the same time a part of their acid, and a basic valerate of mercury remains. *Valerate of Silver*. This salt is obtained in the form of a white caseous precipitate, on mixing the solutions of valerate of potassa and nitrate of silver. It crystallizes from its hot aqueous solution in the form of brilliant scales, very sparingly soluble in cold water, and soon blackening when exposed to light.

*Chlorovaleric Acids*. When chlorine is passed into pure hydrated valeric acid, under the exclusion of daylight, a violent action at first ensues attended by great rise of temperature, so that the acid requires to be cooled by immersion in a freezing mixture. When this has ceased, and the chlorine continuously passed into the liquor till hydrochloric acid is no longer evolved, even on raising the temperature to  $120^{\circ}$  or  $130^{\circ}$ , the resulting product is *chlorovalerisic acid*,  $= C_{10} H_7 O_4 Cl_3$ . To separate from it the residuary chlorine and hydrochloric acid, a stream of dry carbonic acid must be passed through it, at a temperature of about  $175^{\circ}$ .

Chlorovalerisic acid is semifluid, transparent, inodorous, and of a sharp pungent flavor; it does not congeal at  $0^{\circ}$ , and is perfectly fluid at  $85^{\circ}$ . It immediately unites to water, forming a very liquid and almost inodorous combination, heavier than water. When this acid is heated to about  $240^{\circ}$ , it is decomposed, with evolution of hydrochloric gas.

When chlorine is conducted into valeric acid under the influence of sunshine, the same precautions being taken as in the preceding case, a compound in many respects similar to the above is formed, but its formula is  $C_{10} H_6 O_4 Cl_4$ : this has been distinguished as *chlorovalerosic acid*.

In these compounds, the original type of the valeric acid is preserved, and they are each formed by the substitution of chlorine for hydrogen, so that, as suggested by Dumas, they may be represented as follows:



*Valerone*. When basic valerate of lime is subjected to dry distillation, a colorless liquid is obtained, of an agreeable ethereal but somewhat valerianic odor, lighter than, and insoluble in water, but soluble in alcohol and in ether, perfectly neutral, and burning with a bright but sooty flame; its boiling-point is about  $230^{\circ}$ , and the density of its vapor  $= 4.94$ . Its formula is  $C_9 H_9 O$ . (LÖWIG.)

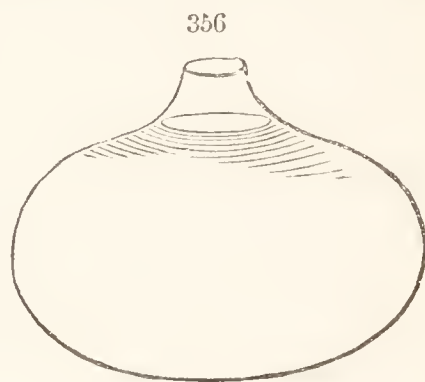
### III. CONCRETE ESSENTIAL OILS. CAMPHORS.

COMMON CAMPHOR.  $C_{10} H_8 O$ . This is the produce of the *Laurus camphora* or *Camphor laurel* of Japan and China, whence it has been introduced into Java. It is extracted from the roots and wood of the

tree, which are chopped up, and boiled with water in an iron vessel to which an earthen head containing straw is adapted; the camphor sublimes, and condenses upon the straw. (THUNBERG. *Flora Japonica*.) In China, the chopped branches are boiled in water till camphor begins to adhere to the stirrer; the liquid is then strained, and the camphor concretes on standing: it is afterwards mixed with a finely powdered earth, and sublimed from one metallic vessel into another. (DAVIS. *The Chinese*, ii. 355.)

There are two kinds of *crude camphor* known in commerce, namely the *ordinary unrefined*, (*China camphor*, *Formosa camphor*,) which is imported from Singapore, Bombay, &c., in chests lined with lead-foil, containing from 1 to  $1\frac{1}{2}$  cwt., and consists of dirty greyish grains; and *Dutch, or Japan camphor*, brought from Batavia in barrels covered with matting, each containing upwards of a hundred weight: it consists of pinkish grains aggregated into masses, and is cleaner and more easy to sublime than the China camphor.

*Refined Camphor* is prepared by sublimation; the process was formerly carried on at Venice, and then in Holland, but is now extensively practised in London. The vessels in which the sublimation is effected, are called *Bombaloes*, and are made of thin flint glass, of the annexed shape, being about a foot in diameter at the widest part; they are filled with the crude camphor, and then embedded in a sand-bath and heated. When the camphor fuses, lime (and according to some, charcoal) is added, and the temperature raised so as to boil the camphor, the vapor of which condenses in the upper part of the vessel. As the sublimation proceeds, the height of the sand round the vessel is diminished, and in about 48 hours the process is usually completed; the vessels are then removed, and cracked by sprinkling them with water. When quite cold, the cake of camphor, which weighs about eleven pounds, is removed, and trimmed, so as to form the hemispherical cakes, perforated in the centre, in which refined camphor occurs in commerce. (PEREIRA, *Mat. Med.*, p. 1151.)



Camphor is a white semi-transparent substance, of a crystalline fracture, of a peculiar odor, and a warm, pungent, and somewhat bitterish flavor, attended by a sense of coldness upon the tongue; it is soft and tough, and cannot be pulverised unless moistened with a few drops of alcohol, when it readily admits of reduction to powder. It evaporates in the air at ordinary temperatures, and gradually sublimes in close vessels, and attaches itself to the surfaces most exposed to light, in small brilliant octohedral crystals, derived, according to W. Phillips, (*PARIS'S Pharmacologia*,) from a right rhombic prism: it also crystallizes when deposited by the slow evaporation of its solution in alcohol. Its sp. gr. is 0.987. When small pieces of camphor are floated upon water, they often rotate in a remarkable manner, in consequence, it is said, of the adhesion of the vapor which emanates from them, to the surface of the water: but the movement ceases when a drop of oil is allowed to fall upon and diffuse over the surface of the water. This evaporation of the camphor seems to take place most rapidly just where the fragment touches the surface of the



water; so that a small column of camphor, rising out of the water, is soon cut across at the surface of the liquid. Camphor fuses at  $347^{\circ}$ , and boils at  $400^{\circ}$ , when it may be distilled without decomposition. The density of camphor-vapor is 5.27. Camphor is very sparingly soluble in water, 1 part of camphor requiring about 1000 of water for solution; from this aqueous solution it is said to be precipitated by potassa, but not by soda, or ammonia. This aqueous solution of camphor is used medicinally, under the name of *camphor julep*. Camphor is very soluble in alcohol, ether, acetone, acetic acid, wood-spirit, and sulphuret of carbon. 100 parts of spirit of wine, of sp. gr. 0.806, dissolve 120 of camphor, (constituting the *camphorated spirit of wine* of Pharmacy,) and the greater part of it is thrown down on the addition of water, in a pulverulent form: it furnishes a ready means of obtaining camphor in a finely-divided state. When a little phosphorus is added to a solution of camphor in its weight of sulphuret of carbon, the liquor separates into two layers as the phosphorus dissolves, which are not miscible; each layer holds in solution a certain quantity of phosphorus and of camphor, but in different proportions; the light portion is soluble in alcohol of sp. gr. 0.848, but not the heavier portion. Camphor increases the solubility of corrosive sublimate in alcohol. Camphor may be united by fusion to sulphur, and to phosphorus. It is very combustible, burning with a bright flame. When camphor-vapor is passed over red-hot iron, it yields a liquid hydrocarbon =  $C_{16}H_8$ , and a portion of naphthaline. (D'ARCET, *Ann. Ch. et Ph.*, LXvi. 118.) Passed over red-hot lime, it yields *camphrone* ( $C_{30}H_{22}O$ ), and water. (FREMY, *Ann. Ch. et Ph.*, Lix. 16.) Passed through a mixture of caustic potassa and lime, heated up to about  $620^{\circ}$ , camphor-vapor forms *campholic acid* =  $C_{20}H_{17}O_3$ , which combines with the potassa. (DE-LALANDE, *Ann. Ch. et Ph.*, 3ème Sér., i. 120 and 368.) Distilled with anhydrous phosphoric acid, camphor is resolved into *camphone* (*Camphogene*, Dumas) =  $C_{10}H_7$ , and water. This camphone combines with fuming sulphuric acid to form *sulphocamphic acid* =  $C_{20}\overset{H_{13}}{SO_2}SO_3$ . (DE-LALANDE.)

The elements of camphor are :

|             | Dumas and Stass. |    |        |        | Blanchet and Sell. |        | Laurent. | Gerhardt. | Rochleder. |
|-------------|------------------|----|--------|--------|--------------------|--------|----------|-----------|------------|
| Carbon .... | 10               | 60 | 78.94  | 79.02  | 78.91              | 79.01  | 78.3     | 78.84     |            |
| Hydrogen    | 8                | 8  | 10.53  | 10.57  | 10.51              | 10.51  | 10.8     | 10.40     |            |
| Oxygen....  | 1                | 8  | 10.53  | 10.41  | 10.58              | 10.48  | 10.9     | 10.76     |            |
| Camphor     | 1                | 76 | 100.00 | 100.00 | 100.00             | 100.00 | 100.0    | 100.00    |            |

The action of *chlorine* upon camphor has not been minutely studied. With *bromine* it forms a crystalline compound =  $C_{10}H_8O + Br$ . (LAURENT. (*Ann. Ch. et Ph.*, LXv. 207.) When equal parts of *iodine* and camphor are rubbed together, a brown semifluid mixture is formed, soluble in alcohol and in ether, and the alkalis throw down camphor from these solutions. When this mixture of iodine and camphor, after having been kept for some days, is heated in a retort, it begins to boil at  $248^{\circ}$ , and hydriodic acid is evolved; the boiling-point then slowly rises to  $322^{\circ}$ , when a brown liquid distils over, leaving a black resin-like substance in the retort. The distillate separates into two layers; the uppermost, and lightest, consisting chiefly of *camphine* ( $C_{18}H_{11}$ ), and the lower-

most of hydriodic acid, iodine, and camphor. (CLAUS. *Bulletin Scientifique de St. Petersbourg*, ix. 229.)

Camphor absorbs 144 times its volume of *hydrochloric gas* (at the temperature of  $50^{\circ}$ ), and forms a transparent colorless liquid, which is a *hydrochlorate of camphor*; it is immediately decomposed by water, and camphor is precipitated.

When camphor is digested for two or three days, with about thrice its weight of *sulphuric acid*, at the temperature of  $212^{\circ}$ , and water then added to the mixture, an oil floats upon the surface, which, when purified, is of the same composition as camphor, and which resumes the form of camphor when acted upon by caustic potassa. If a mixture of camphor with 4 parts of sulphuric acid be subjected to distillation in a retort, dilute sulphuric and sulphurous acid pass over, together with a yellow volatile oil having the odor of a mixture of the oils of lavender and peppermint rather than of camphor. The residue in the retort, when acted upon by water, leaves charcoal, and a mixture of sulphuric acid and artificial tannine is dissolved. (HATCHETT, *Phil. Trans.*, 1805. See also a paper on the action of sulphuric acid on camphor by Chevreul. *Annales de Chimie*, lxxiii. 157.)

*Nitric acid* dissolves camphor, and produces what was formerly termed *oil of camphor*; it appears to be a *nitrate of camphor*; it is immediately decomposed by water; if the camphor and acid be heated together, *camphoric acid* is ultimately formed.

*Camphoric Acid.*  $C_{10}H_7O_3 + HO = \overline{\text{Cam}} + HO$ . The production of a crystalline acid by the protracted action of nitric acid upon camphor, was first observed by Kosegarten (*de Camphorá*, &c., 1785); the process was improved by Bouillon-Lagrange (*Annales de Chimie*, xxiii. 153, xxvii. 19), by Bucholz (*Gehlen's Journ.*, ix. 339,) and by Brandes, (*Schweigger's Journ.*, xxxviii. 269.) Camphoric acid is best obtained by distilling 4 ounces of pulverised camphor with 30 ounces of common concentrated nitric acid, in a two-quart tubulated retort placed in a sand-heat: when two-thirds of the acid have passed over, return it into the retort and distil as before, repeating the operation twice more, after which, as the liquor cools, crystals of camphoric acid are deposited, which are to be washed, and dried. During this operation nitric oxide is abundantly evolved, but no carbonic acid; showing that the camphor is not decomposed, but oxidized. Before the conversion of the camphor into camphoric acid is complete, certain intermediate compounds of camphor and camphoric acid appear to be formed, (*camphorates of camphor*), together with the *nitrate of camphor* above adverted to; so that the distillations should be repeated till red fumes are no longer produced. The crystals of camphoric acid first formed should be redissolved and recrystallized from boiling water, two or three times successively.

*Hydrated Camphoric Acid*, thus obtained, forms small lamellar crystals of a slightly sour and bitterish taste; it fuses at  $145^{\circ}$ , and when subjected to dry distillation, is resolved into water and *anhydrous camphoric acid*, a small portion of carbonaceous matter being always at the same time set free. The hydrated acid is very little soluble in cold water; boiling water takes it up to the amount of about 12 *per cent.*, but the greater part is deposited on cooling the solution: it is very soluble in alcohol, and in ether, and hot oil of turpentine.



*Anhydrous Camphoric Acid* is obtained by washing the sublimate formed during the dry distillation of the hydrated acid, with cold alcohol, then dissolving it in boiling alcohol, and suffering it to crystallize. It forms colorless brilliant flattened prisms, the sp. gr. of which at  $70^{\circ}$  is 1.194. (LIEBIG, *Ann. Ch. et Ph.*, XLVII. 95.) It is not acid, and almost tasteless, but after a time produces a sense of irritation in the throat, resembling that occasioned by benzoic acid. It is scarcely soluble in cold water, but boiling water dissolves it more abundantly, and the saturated solution deposits the excess of acid, on cooling, in white *anhydrous* crystals, which, according to Malaguti (*Ann. Ch. et Ph.*, LXIV. 151,) may be boiled with water for 12 hours without becoming hydrated; but after protracted ebullition beyond that period, they ultimately revert to the state of hydrate. (LAURENT, *Ann. Ch. et Ph.*, LXIII. 207.) Although camphoric acid is not much more soluble in cold alcohol than in water, boiling alcohol takes it up in considerable quantity, and it is even more abundantly soluble in ether. At a temperature of  $266^{\circ}$ , the anhydrous camphoric acid begins to sublime in white needles; at  $425^{\circ}$  it fuses into a colorless liquid; and at  $518^{\circ}$  it boils and distils over, unchanged; the density of its vapor is 6.329. It is strongly electrical when triturated in a glass or porcelain mortar. It is soluble without decomposition in cold fuming sulphuric acid, and is thrown down from it by water; but if the solution be heated, carbonic oxide is evolved, and a new acid (*sulphocamphoric acid*,  $= C_9 H_7 O_5 S$ ) is formed. ( $C_{10} H_7 O_3 + SO_3 = C_9 H_7 O_5 S + CO$ . WALTER, *Ann. Ch. et Ph.*, LXXIV. 38, LXXV. 212. *Ibid*, 3ème Sér., ix. 177.)

The equivalent of *anhydrous camphoric acid* is 91, its components being

|                          | Laurent. |    |        | Malaguti. |        |        | Liebig. |        |        |
|--------------------------|----------|----|--------|-----------|--------|--------|---------|--------|--------|
| Carbon.....              | 10       | 60 | 65.93  | 65.37     | 66.24  | 66.37  | 66.37   | 66.37  | 66.37  |
| Hydrogen .....           | 7        | 7  | 7.69   | 7.84      | 7.90   | 7.84   | 7.84    | 7.84   | 7.84   |
| Oxygen .....             | 3        | 24 | 26.38  | 26.79     | 25.86  | 25.79  | 25.79   | 25.79  | 25.79  |
| Anhydrous camphoric acid | 1        | 91 | 100.00 | 100.00    | 100.00 | 100.00 | 100.00  | 100.00 | 100.00 |

The equivalent of the *crystallized camphoric acid* is 100; its ultimate elements are

|                             | Laurent. |     |        | Malaguti. |       |       | Liebig.  |  |  |
|-----------------------------|----------|-----|--------|-----------|-------|-------|--|--|--|
| Carbon .....                | 10       | 60  | 60.10  | 60.20     | 60.5  | 60.5  | } = { Anhydrous<br>camphoric<br>acid .....<br>Water .....<br>1 ..... 9 |  |  |
| Hydrogen .....              | 8        | 8   | 8.16   | 8.00      | 8.0   | 8.0   |  |  |  |
| Oxygen .....                | 4        | 32  | 31.74  | 31.80     | 31.5  | 31.5  |  |  |  |
| Hydrated camphoric acid.... | 1        | 100 | 100.00 | 100.00    | 100.0 | 100.0 | 1 100  |  |  |

Liebig doubts the existence of anhydrous organic acids, and observes that their introduction has arisen out of our ignorance respecting the real constitution of the hydrates of those acids. "The action of heat upon emetic tartar, and the existence of polybasic succinates of lead, discovered by Fehling, clearly proved that the substances called anhydrous tartaric, and anhydrous succinic acid, contain a certain quantity of water, which certain bases are capable of eliminating; and anhydrous camphoric acid is doubtless in the same predicament. All the so-called *anhydrous acids* are in the same relation to their hydrates, as the phosphoric and

metaphosphoric acid; at least the experiments of Malaguti demonstrate that the salts of the anhydrous camphoric acid are possessed of properties distinct from those of the salts of the ordinary, or hydrated acid." (*Chim. Org.*, ii. 140.)

The salts of the anhydrous camphoric acid differ, in several respects, from those of the hydrated acid. An alcoholic solution of the anhydrous acid does not precipitate acetate of lead; and the ammonia-salt of the anhydrous acid forms no precipitate in the solutions of copper, lead, or silver. This *ammonia-salt* is formed by dissolving the anhydrous acid in caustic, or in carbonated ammonia, and evaporating by a gentle heat; a syrupy liquor is obtained, which after some days concretes into a crystalline mass, the composition of which is expressed by  $\text{NH}_4, \text{O} + \text{C}_{10} \text{H}_7 \text{O}_3 = \text{C}_{10} \text{H}_{11} \text{O}_4 \text{N}$ . This salt fuses at  $212^\circ$ , and is easily soluble in water; when decomposed by the acids, it is not anhydrous camphoric acid which is precipitated, but an acid resin-like substance, which soon hardens, and is very soluble in alcohol; and although the potassa-salt of the anhydrous acid resembles that of the hydrated acid in its general chemical properties, it crystallizes in large nacreous plates instead of needles.

*Camphorates of the Hydrated Acid. Common Camphorates. Camphorate of Ammonia.* Hydrated camphoric acid absorbs gaseous ammonia, and when saturated, the ammonia-salt may be crystallized in needles from its aqueous solution: on the addition of acids, the unchanged hydrated acid is precipitated. This salt gives pulverulent precipitates with solutions of the salts of copper, lead, and silver, by which it is remarkably distinguished from the corresponding (isomeric) salt of the anhydrous acid. When a boiling solution of hydrated camphoric acid is saturated by bicarbonate of ammonia, white prismatic crystals separate on cooling, which are  $= 2[\text{NH}_4 \text{O}] + 3[\text{C}_{10} \text{H}_7 \text{O}_3] + 10\text{HO}$ . In a dry air they lose 9 atoms of water. This salt is very soluble in water, and precipitates nitrate of lead and sulphate of copper. (MALAGUTI.) *Camphorate of Potassa* forms delicate acicular crystals, of an aromatic bitterish taste; they contain water of crystallization, which may be expelled by heat. *Camphorate of Soda* forms cauliflower excrescences, which are deliquescent, but require 75 parts of alcohol for solution. *Camphorate of Baryta* and of *Strontia* form delicate acicular and lamellar crystals. *Camphorate of Lime* crystallizes in large 4-sided prisms, which contain 8 atoms of water: they dissolve in 4 parts of cold water. *Camphorate of Magnesia* also forms 4-sided prisms, soluble in 6.5 parts of water, and in 50 of alcohol. *Camphorate of Manganese* is very soluble, and crystallizes in small scales. *Camphorate of peroxide of Iron* forms a bulky red-brown precipitate. *Camphorate of Zinc* is thrown down in the form of a white powder. *Camphorate of Nickel* is grey, and difficultly soluble. *Camphorate of Copper.* Solution of sulphate of copper dropped into a solution of neutral camphorate of ammonia, gives a pale green precipitate. *Camphorate of Mercury* is a grey precipitate. *Camphorate of Silver*, from camphorate of potassa and nitrate of silver, is white. *Camphorate of Platinum*, yellow, and difficultly soluble.

BORNEO-CAMPHOR.  $\text{C}_{10} \text{H}_9 \text{O}$ . This substance is the produce of the *Driabalanops Camphora*, or *aromatica*, the *camphor-tree* of Sumatra and Borneo, which also produces a liquid called *camphor-oil*  $= \text{C}_{10} \text{H}_8$ .



*Borneo-camphor.* According to Marsden, (*Hist. of Sumatra*, 151,) the young trees produce the oil, and the old ones the camphor, which is found in the natural fissures of the wood, and obtained by cutting down the tree, and splitting it into small pieces, so as to discover the crevices in which the camphor has been deposited; it is highly esteemed by the Chinese, who assign most extravagant virtues to it. It very rarely comes to this country as an article of commerce: it occurs in small white fragments of crystals, transparent, brittle, and of a camphoraceous and pepper-like odor, and hot taste; it is lighter than, and only very slightly soluble in water; very soluble in alcohol, and in ether; fusible, and volatile. It is distinguished, by several characters, from common or laurel-camphor; such as the prismatic form of its crystals, their greater hardness and brittleness, and their inferior tendency to vaporization. (PEREIRA, *Mat. Med.*, p. 1694.) It is produced artificially, by boiling the above-mentioned *camphor-oil* with solution of potassa, in which case the oil unites to the elements of water to form the camphor, as will be evident from the above-cited formulæ of the camphor and of the oil, deduced from the following analyses: Pelouze examined the native camphor, (*Journ. de Pharm.*, xxvi. 645,) and Gerhardt, that formed from the oil. (*Ann. Ch. et Ph.*, 3ème Sér., vii. 288.) The latter chemist calls the camphor *Bornééne*; and the oil, *Bornéole*.

|                      |    |      |    |      |        | Pelouze and Gerhardt. |        |            |
|----------------------|----|------|----|------|--------|-----------------------|--------|------------|
| Carbon.....          | 10 | .... | 60 | .... | 77.92  | ....                  | 77.68  | .... 77.59 |
| Hydrogen .....       | 9  | .... | 9  | .... | 11.69  | ....                  | 11.99  | .... 11.73 |
| Oxygen .....         | 1  | .... | 8  | .... | 10.39  | ....                  | 10.33  | .... 10.68 |
| <hr/>                |    |      |    |      |        | <hr/>                 |        |            |
| Borneo-camphor ..... | 1  |      | 77 |      | 100.00 |                       | 100.00 | 100.00     |

*Camphor-oil.*  $C_{10}H_8$ . *Liquid camphor.* This oil is obtained by making incisions into the tree, from which the oil issues. It is occasionally imported into this country in tin canisters: it is sometimes perfectly limpid and colorless, but more generally yellow or brown; its odor resembles that of cajeput oil mixed with that of camphor and cardamoms: some samples smell of turpentine. It was first analyzed by Martius and Ricker, who found the *crude oil* composed of  $C_{10}H_8O_4$ , (*Ann. der Pharm.*, xxvii. 65,) but afterwards Mulder, (*Ibid.*, xxxi. 67) and Gerhardt, showed it to be a mixture of camphor and a hydrocarbon  $= C_{10}H_8$ . According to Brandes, the *volatile oil of laurel-berries*, when purified by distillation off caustic potassa, is of the same composition; as is also the hydrocarbon of *valerian oil*. The sp. gr. of crude camphor-oil is about 0.945; that of the rectified oil 0.919: the density of its vapor is 4.73. (GERHARDT.)

By the action of nitric acid, camphor-oil is converted into camphor. When dissolved in an alcoholic solution of caustic potassa, and, after some days, mixed with water, a portion of camphor (Borneo-camphor  $= C_{10}H_9O$ ) separates. The term *Bornéole* (and sometimes *Bornééne*) has been applied by Gerhardt and some other chemists to the hydrocarbon of valerian oil, and of laurel oil, as well as to that of camphor oil; and in reference to the conversions of these oils into the two kinds of camphor, Löwig observes that they are best explained by representing *common camphor* by the formula  $C_{10}H_7 + HO$ , and *Borneo-camphor* by  $C_{10}H_8 + HO$ .

**HELENINE.** *Elecampane-camphor.*  $C_{21}H_{14}O_3$ . This substance was discovered by Geoffroy, (*Mem. de l'Acad.*, 1721, p. 155,) and was afterwards examined by Dr. Lewis, (*Transl. of Neumann's Chem.*, 420.) It has been more recently described and analyzed by Dumas, (*Journ. de Pharm.*, xxi. 192,) and by Gerhardt, (*Ann. Ch. et Ph.*, lxxii., 163.) Helenine (which must not be confounded with *Inuline*, an amylaceous principle existing in the same plant, p. 1168,) exists ready formed in the root of *elecampane* (*Inula Helenium*), an indigenous plant, formerly much employed as an aromatic tonic, especially in pulmonary affections. It may be seen, by the help of the microscope, lining the cellular cavities of the root, in the form of a crystalline deposit; and is obtained, either by distilling the bruised root with water, or digesting it in hot alcohol; in the former case it passes over in the form of a yellow oil, which soon concretes: in the latter, it crystallizes on cooling, and may be purified by again dissolving and crystallizing. It then forms white quadrilateral prisms, lighter than water, of a slight taste, insoluble in water, but very soluble in alcohol and in ether, in essential oils, and in kreasote: it fuses at  $160^{\circ}$ , and boils at about  $530^{\circ}$ : its vapor has a peculiar odor, somewhat resembling that of *patchouli*; but at this temperature it undergoes a change, so that its density cannot be ascertained. When helenine is slowly fused, it crystallizes on cooling; but if kept for some time in fusion, it concretes into a resin-like mass. When heated in solution of potassa, it fuses, and then dissolves, and is thrown down again by an acid; but it is decomposed when fused with caustic potassa. Distilled with lime, it yields a yellow inflammable liquid. Sulphuric acid dissolves it without the evolution of sulphurous acid, forming a solution which is at first red, but afterwards blackens: a combination remains in solution, which Gerhardt terms *sulphohelenic acid*. Helenine is not affected by chlorine, even under the influence of light, unless heated, when hydrochloric acid is formed, together with a resinous product, in which a certain number of atoms of hydrogen are replaced by their equivalent of chlorine. It absorbs hydrochloric gas, and forms with it a bluish liquid compound. It dissolves in cold nitric acid, and is thrown down, without change, on the addition of water; but if the solution be heated, an azotized resin (*nitrohelenine*) is produced. When a mixture of helenine and anhydrous phosphoric acid is distilled, an oily product is obtained, which has been termed *helenène*, and to which Gerhardt assigns the formula  $C_{19}H_{13}$ .

The components of helenine are

|                |    |     |     |     |        |     | Dumas. |     |       |  | Gerhardt. |
|----------------|----|-----|-----|-----|--------|-----|--------|-----|-------|--|-----------|
| Carbon .....   | 21 | ... | 126 | ... | 76.83  | ... | 76.9   | ... | 76.2  |  |           |
| Hydrogen ..... | 14 | ... | 14  | ... | 8.53   | ... | 8.8    | ... | 8.8   |  |           |
| Oxygen .....   | 3  | ... | 24  | ... | 14.64  | ... | 14.3   | ... | 15.0  |  |           |
| <hr/>          |    |     |     |     |        |     |        |     |       |  |           |
| Helenine ..... | 1  |     | 164 |     | 100.00 |     | 100.0  |     | 100.0 |  |           |

The formula originally assigned to helenine by Gerhardt, was  $C_{15}H_{10}O_2$ .

**ASARINE.** *Asarabacca-camphor.*  $C_{20}H_{13}O_5$ . This substance was discovered by Lassaigne and Feneulle (*Journ. de Pharm.*, vi. 561) in the roots of common *asaarabacca* (*Asarum Europæum*.) It has been



examined by Graeger, (*Dissert. de Asaro Europ.*, &c., Göttingen, 1830) by Blanchet and Sell, (*Ann. der Pharm.*, vi. 297,) and lastly by Schmidt, (*Ibid.*, Liii. 156.) To obtain it, the root is distilled with water, when an oil passes over which soon concretes: when this is dissolved in alcohol, and water added to the solution, crystals of *asarite* are separated, and float about in the liquor; at the same time an oil-like matter falls to the bottom, which, after some time, concretes into a mixture of *asarine* and *asarum oil*; these may be separated from each other by careful pressure between folds of bibulous paper.

*Asarine* is a white, transparent, crystalline substance, fusible at 104°, and again concreting at 80°. It boils at about 540°, and at 570° begins to be decomposed. When its alcoholic solution is boiled for 15 or 20 minutes, it reddens, and on cooling, a part of the asarine crystallizes, and part is converted into a red resinous substance, which, on evaporation, remains amorphous, but appears to be of the same composition as the original asarine. The components of asarine are

|                |    |      |     |      |        | Schmidt. |        | Blanchet and Sell. |        |
|----------------|----|------|-----|------|--------|----------|--------|--------------------|--------|
| Carbon .....   | 20 | .... | 120 | .... | 69·36  | ....     | 69·40  | ....               | 69·27  |
| Hydrogen ..... | 13 | .... | 13  | .... | 7·56   | ....     | 7·66   | ....               | 7·67   |
| Oxygen .....   | 5  | .... | 40  | .... | 23·08  | ....     | 22·94  | ....               | 23·06  |
| <hr/>          |    |      |     |      |        |          |        |                    |        |
| Asarine .....  | 1  |      | 173 |      | 100·00 |          | 100·00 |                    | 100·00 |

*Asarite* forms small silky crystals, lighter than and insoluble in water, but soluble in alcohol, ether, and oils; it appears, as far as it has been examined, closely to resemble asarine. The *oil of asarum* has an odor resembling valerian, and is probably a mixture of a hydrocarbon and a camphor.

ANEMONINE. *Anemone-camphor*. C<sub>15</sub> H<sub>6</sub> O<sub>6</sub>. This substance, discovered by Heyer (*Crell's Annalen*, ii. 102), has been examined by Robert and Vauquelin, (*Journ. de Pharm.*, vi. 229) by Schwartz, (*Mag. Pharm.*, x. 193 and xix. 168,) and more especially by Fehling (*Ann. der Pharm.*, xxxviii. 278.) It is obtained by distilling the fresh leaves of *Anemone pulsatilla*, *pratensis*, or *nemorosa*, with 2·5 parts of water, till 1 part has passed over. This distillate is then put into a retort, and one-fifth of it distilled off, from which, after having been set aside for some weeks in a cool place, crystals of anemonine separate. According to Schwartz, this formation of the camphor arises out of the combination of the elements of water with a peculiar essential oil.

*Anemonine* forms acicular crystals, little soluble in cold, but abundantly in boiling alcohol, and very little soluble either in water or in ether. It is heavier than water; and though at first it appears to be tasteless, it produces after some time an acrid and benumbing sensation upon the tongue, which lasts for some days. Heated to about 300° it softens, but does not fuse; it then exhales an acrid vapor, and at 570° is decomposed, leaving a carbonaceous residue. It forms, according to Fehling, definite compounds with oxide of lead, and oxide of silver; and when boiled in excess of baryta water, is converted into *anemonous acid*, = C<sub>9</sub> O<sub>4</sub> O<sub>4</sub>. According to Schwartz, the water distilled off *Anemone nemorosa* contains, together with anemonine, a difficultly soluble substance, which is volatile, and combines with acids, forming two distinct

sets of salts; he has termed it *anemonic acid*, and represents it as composed of  $C_{15}H_7O_7$ . Anemonine consists of

|                 |    |      |     |      |        |      |                    |
|-----------------|----|------|-----|------|--------|------|--------------------|
| Carbon .....    | 15 | .... | 90  | .... | 62.50  | .... | Fehling.<br>62.879 |
| Hydrogen .....  | 6  | .... | 6   | .... | 4.16   | .... | 4.169              |
| Oxygen .....    | 6  | .... | 48  | .... | 33.34  | .... | 32.952             |
| <hr/>           |    |      |     |      |        |      |                    |
| Anemonine ..... | 1  |      | 144 |      | 100.00 |      | 100.000            |

COUMARINE. *Tonka-camphor*. *Coumarylic acid*.  $C_{18}H_7O_4$ . This substance has been studied by Boullay and Boutron-Charlard (*Journ. de Pharm.*, xi. 480,) and by Delalande, (*Ann. Ch. et Ph.*, 3ème Sér., vi. 343.) It is extracted from the *Tonka bean* (the fruit of *Coumarouna odorata*,) and from the flowers of *Melilot* (*Melilotus officinalis*): to obtain it, the Tonka beans are sliced, and digested in alcohol, sp. gr. 0.837. The liquor is then evaporated to the consistence of syrup, and on cooling it deposits small yellowish prismatic crystals, which may be purified by recrystallization. The purified crystals are white, hard, of an agreeable aromatic odor and hot flavor, scarcely soluble in cold water, but soluble in boiling water, which on cooling deposits it in the form of silky acicular crystals. The dilute acids dissolve it without change. Sulphuric acid chars it. With strong nitric acid it forms at first a crystallizable product (*nitro-coumarine*,) and by long boiling yields carbazotic acid. Hydrochloric acid has no effect upon it. It is not changed by ammonia: gently heated with solution of potassa, it yields a yellow solution, from which it is at first precipitated by the acids, but on boiling it with concentrated solution of potassa, water is decomposed, hydrogen evolved, and the coumarine, acquiring an atom of oxygen, is converted into *coumaric acid*,  $= C_{18}H_7O_5$ . When fused with potassa, it undergoes further change; hydrogen is evolved, and the coumaric acid then loses 4 atoms of carbon and 2 atoms of hydrogen, and is converted into *salicylic acid*. Coumarine has no action on the metallic salts: it forms crystallizable compounds with chlorine, iodine, and bromine. Coumarine consists of

|                 |    |      |     |      |        |      |                    |
|-----------------|----|------|-----|------|--------|------|--------------------|
| Carbon .....    | 18 | .... | 108 | .... | 73.47  | .... | Delalande.<br>73.7 |
| Hydrogen .....  | 7  | .... | 7   | .... | 4.76   | .... | 4.7                |
| Oxygen .....    | 4  | .... | 32  | .... | 21.77  | .... | 21.6               |
| <hr/>           |    |      |     |      |        |      |                    |
| Coumarine ..... | 1  |      | 147 |      | 100.00 |      | 100.0              |

Delalande has pointed out the relations which subsist between the *cinnamic* and the *coumaric series*, and between these and the *benzoic* and *salicylic series*, in the following table; showing, that the radical of the cinnamic and coumaric series  $= C_{18}H_7$ , passes into the radical of the benzoic and salicylic series, by the loss of 4 atoms of carbon and 2 of hydrogen.

|                     |                |                  |                    |                |
|---------------------|----------------|------------------|--------------------|----------------|
| Cinnamyle.....      | $C_{18}H_7O_2$ | } - $C_4H_2$ = { | Benzoyle.....      | $C_{14}H_5O_2$ |
| Cinnamic acid ..... | $C_{18}H_7O_3$ |                  | Benzoic acid ...   | $C_{14}H_5O_3$ |
| Coumarine .....     | $C_{18}H_7O_4$ |                  | Salicyle .....     | $C_{14}H_5O_4$ |
| Coumaric acid ..... | $C_{18}H_7O_5$ |                  | Salicylic acid ... | $C_{14}H_5O_5$ |

Many essential oils and camphors have been described, which are not included in the preceding list; some of these have been, or will be men-



tioned, elsewhere; and as respects the omitted essential oils, they have been shown, with very few exceptions, to be mixtures of hydrocarbons and oxyhydrocarbons, the types of which, together with their most important varieties, have been enumerated in the foregoing pages.

#### IV. ESSENTIAL OILS CONTAINING NITROGEN AND SULPHUR.

**OIL OF BLACK MUSTARD SEED.**  $C_8 H_5 N S_2$ . To obtain this oil, the cake of the seed, after the fixed oil has been expressed, is made into a paste with water, which after some hours is subjected to distillation, in the same way as bitter-almond oil is distilled from the almond-cake; and as in that case the oil is *formed* by the action of emulsine upon amygdaline, so in the present instance, the volatile mustard-oil is formed by the action of a substance analogous to emulsine, which has been termed *myrosine*, upon a peculiar substance existing in the black mustard seed, and which has been termed *myronic acid*, *sulphosinapisine*, and *sinapine*: the term *sulphosinapine* may perhaps be most appropriately applied to this principle, which corresponds to *amygdaline* in bitter almonds, and which, under the influence of myrosine, water, and a proper temperature, produces the volatile oil of mustard. The oil which first passes over with the water requires to be redistilled with water, then dehydrated by means of fused chloride of calcium, and lastly rectified by distillation alone.

The oil, thus purified, is a colorless liquid of a strong pungent odor, and a burning flavor; it immediately blisters the skin; its sp. gr. is about 1.015; its refractive power is  $= 1.516$ ; it is very soluble in alcohol and in ether, and water separates it from them. It boils at  $290^\circ$ , and the density of its vapor is 3.44. (DUMAS and PELOUZE.) By the aid of heat, it dissolves sulphur, which crystallizes as the solution cools; in the same way it also dissolves a considerable proportion of phosphorus.

This oil has been examined by Dumas and Pelouze (*Ann. Ch. et Ph.*, liii. 182), by Robiquet and Bussy (*Ibid.*, lxxii. 328), by Simon (*Poggend. Ann.*, L. 337), by Will (*Ann. der Pharm.*, lii. 1; *Chem. Gaz.*, 1845, pp. 253, 277), and by Löwig (*Chimie der Org. verbind.*, ii. 1439). The following are the results of its analysis:

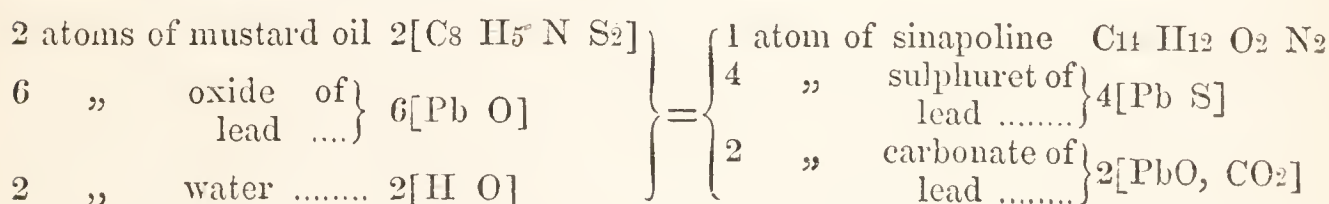
|   |   |     |    |     | Will.  | Löwig. |        |     |        |
|---|---|-----|----|-----|--------|--------|--------|-----|--------|
| Carbon .....                            | 8 | ... | 48 | ... | 48·48  | ...    | 48·68  | ... | 49·25  |
| Hydrogen .....                          | 5 | ... | 5  | ... | 5·05   | ...    | 5·39   | ... | 5·21   |
| Nitrogen .....                          | 1 | ... | 14 | ... | 14·14  | ...    | 14·12  | ... | 14·45  |
| Sulphur.....                            | 2 | ... | 32 | ... | 32·33  | ...    | 31·81  | ... | 31·09  |
| <hr/>                                   |   |     |    |     |        |        |        |     |        |
| Volatile oil of black mustard seed .... | 1 |     | 99 |     | 100·00 |        | 100·00 |     | 100·00 |

If we consider this oil as containing sulphocyanogen, it may be regarded as a compound of that substance with a hydrocarbon  $= C_6 H_5$ , or *allyle*; that is, as a *sulphocyanide of allyle*,  $= C_6 H_5 + C_2 NS_2$ ; and there are certain properties of this oil, and of its congener, the *oil of garlic*, which render this view of its constitution convenient.

When mustard oil is mixed with nitric acid, heat is evolved and there is a production of nitrous acid, and of a yellow substance, (*nitrosinapic resin*,  $= C_{24} H_{12} N_3 S_4 + 3NO_4$ ), which, by the further action of the nitric acid, yields sulphuric acid and *nitrosinapic acid*,  $= C_{18} H_9 N_3 S$

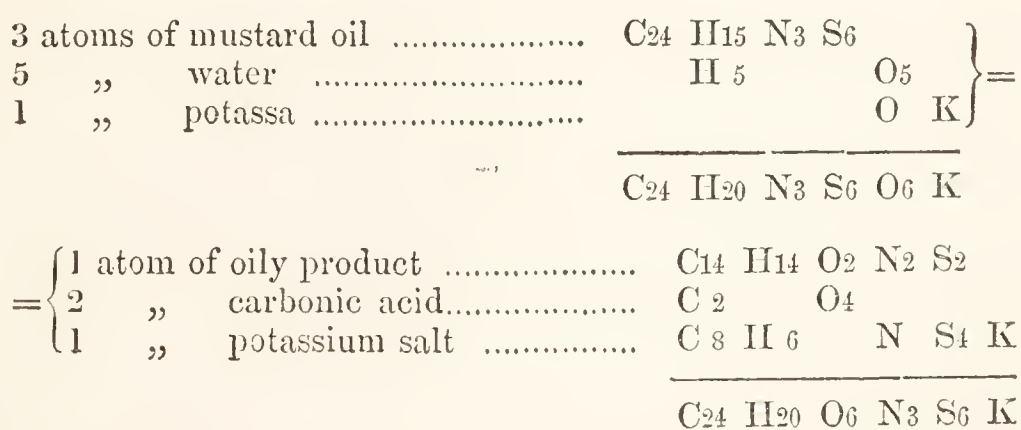
+  $3\text{NO}_4 + \text{NO}_5$ ; and ultimately, the whole of the sulphur may be acidified. (LÖWIG.)

Heated with great excess of baryta water, mustard oil yields a precipitate of carbonate of baryta, and a solution of sulphuret of barium, together with an organic basis, *sinapoline*, =  $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2$ . The oil undergoes the same decomposition when treated with an alkaline solution of hydrated oxide of lead; carbonate of lead, sulphuret of lead, and sinapoline, are the results. (SIMON.)



When mustard oil is mixed with thrice its volume of a strong aqueous solution of caustic ammonia, the odor of the oil gradually vanishes, and at length the whole concretes into a crystalline mass. In this case, a new substance is formed, called by Dumas and Pelouze *thiosinammine*, =  $\text{C}_8\text{H}_8\text{N}_2\text{S}_2$ ; it has the characteristic property of producing definite combinations with chloride of mercury, nitrate of silver, and chloride of platinum. In its formation, 1 atom of the oil,  $\text{C}_8\text{H}_5\text{N}_2\text{S}_2$ , combines with 1 of ammonia,  $\text{NH}_3$ , to form 1 of thiosinammine,  $\text{C}_8\text{H}_8\text{N}_2\text{S}_2$ .

On dropping mustard oil into a concentrated solution of caustic potassa in absolute alcohol, a violent action ensues, which requires to be tempered by the application of cold; the odor of the oil disappears, and carbonate of potassa is formed, together with an oily substance, which is retained in solution by the alcohol, and precipitable by water, and is composed of  $\text{C}_{14}\text{H}_{14}\text{O}_2\text{N}_2\text{S}_2$ ; there is also at the same time produced a potassium salt of a peculiar sulphur acid, which forms a combination with lead, =  $\text{C}_8\text{H}_6\text{N}_2\text{S}_4\text{Pb}$ , indicating the composition of the isolated acid as =  $\text{C}_8\text{H}_6\text{N}_2\text{S}_4$ .



An aqueous solution of mustard oil does not redden the persalts of iron; with the salts of silver it produces a dark-brown precipitate; with protonitrate of mercury the precipitate, at first white, soon becomes gray. An alcoholic solution of the oil produces a peculiar precipitate in a solution of corrosive sublimate, the composition of which has not been accurately determined; nor has the crystallizable combination of the oil with chloride of platinum been minutely examined. (LÖWIG.)

{ The volatile oils of *Alliaria officinalis* (*Erysimum alliaria*), of scurvy grass (*Cochlearia officinalis*), and of horseradish (*Cochlearia armoracia*) appear closely allied to the volatile oil of black mustard.



**OIL OF GARLIC.** This oil is obtained by distilling the *bulbs of garlic* (*Allium sativum*) with water; the greater part of the oil passes over with the first portions of water, to the amount of from 3 to 4 ounces from the hundred-weight of garlic. It is a brown oily liquid, heavier than water, and having an intensely nauseous garlic odor. When this crude oil is heated up to its boiling-point (about  $300^{\circ}$ ), its temperature suddenly rises, accompanied by its continuous decomposition, and the evolution of an insupportably suffocating vapor; a viscid brown substance remains in the retort. In order to purify or rectify the crude oil, it must be distilled in a bath of salt and water, when the more volatile portion of the oil readily passes over, without boiling; it is now lighter than water, and may be boiled without decomposition; it has a pale yellow color, and its odor is less disagreeable than that of the crude oil; if the distillation be continued till nothing further goes over, a thick dark-brown matter remains in the retort, of a nauseous odor. The crude oil yields about two-thirds of its weight of the rectified product.

Wertheim, who has principally examined this oil (*Ann. der Pharm.*, li. 289; lii. 52; lv. 297; *Chem. Gaz.*, 1845, pp. 177, 186, 495;) regards it as a mixture of *oxide of allyle*,  $C_6H_5O$ , with *sulphuret of allyle*,  $C_6H_5S$ .

Rectified garlic oil is very little soluble in water, but abundantly soluble in alcohol and in ether. It is violently decomposed by fuming nitric acid, and when the action has ended, sulphuric and oxalic acid are found in the residue. With sulphuric acid it forms a red solution, from which it is separated, apparently unchanged, by water. It absorbs hydrochloric gas, forming a blue solution, which loses its color by exposure to air, and by dilution with water. Heated with caustic potassa, it evolves no ammonia. When acted upon by potassium, it forms sulphuret of potassium, in combination with a resin-like product, and a small quantity of inflammable gas is evolved; if when this action has ceased, the oil be distilled, pure *sulphuret of allyle* passes over.

Sulphuret of allyle is a clear colorless liquid, powerfully refracting light, of a garlic odor, lighter than, and very sparingly soluble in, water, but readily soluble in alcohol and in ether. The density of its vapor is 3.964. It may also be obtained by heating mustard oil in a sealed tube, with sulphuret of potassium, when sulphocyanide of potassium is also formed.

Sulphuret of allyle consists of

|                           | Wertheim. |      |    |      |        |            |
|---------------------------|-----------|------|----|------|--------|------------|
| Carbon .....              | 6         | .... | 36 | ..   | 63.16  | .... 63.43 |
| Hydrogen .....            | 5         | .... | 5  | .... | 8.79   | .... 8.78  |
| Sulphur .....             | 1         | .... | 16 | .... | 28.05  | .... 27.79 |
| <hr/>                     |           |      |    |      |        |            |
| Sulphuret of allyle ..... | 1         |      | 57 |      | 100.00 | 100.00     |

Sulphuret of allyle combines with many of the metallic sulphurets to form peculiar sulphur-salts, in which it appears as a basis. Of these compounds, the sulphuret of allyle and platinum,  $= C_6H_5S + PtS_2$ , and the palladium compound,  $= C_6H_5S + 3PdS$ , have been analyzed by Wertheim: they are brown insoluble substances.

*Oxide of Allyle.*  $C_6H_5O$ . When *rectified oil of garlic* is added to an excess of a concentrated alcoholic solution of nitrate of silver, sul-

phuret of silver, and a crystalline compound, are formed. If, after 24 hours, the liquor be boiled with the precipitate, and filtered while hot, groups of prismatic crystals separate as it cools, which blacken by exposure to light, and explode when heated, leaving metallic silver. When this compound is dissolved in ammonia, drops of an oil, having a peculiar odor, collect upon the surface of the liquid. This oil is *oxide of allyle*, and when a drop of the solution of nitrate of silver is added to it, the crystalline compound is immediately reproduced. Oxide of allyle may also be obtained by the action of a mixture of soda and lime upon mustard oil, in an hermetically sealed glass tube, bent at a right angle, and carefully heated in an oil-bath to about  $248^{\circ}$ ; the tube must be so placed that the distillate constantly flows back upon the mixture of soda and lime. If, when the reaction is complete, the tube be so placed as to collect the distillate in the empty limb, a colorless oily liquid is obtained which is oxide of allyle, and sulphocyanide of sodium remains. In this case, therefore, the sulphocyanide of allyle (mustard oil) is decomposed as follows.  $C_6H_5 + C_2NS_2 + NaO; = C_6H_5O + Na, CyS_2$ .

Oxide of allyle is a colorless oily liquid of a peculiar disagreeable odor, and eagerly absorbing oxygen from the atmosphere, so as to render it very difficult to obtain it pure. The density of its vapor is 3.41. It consists of

|                       |   |      |    |      |        |
|-----------------------|---|------|----|------|--------|
| Carbon .....          | 6 | .... | 36 | .... | 73.47  |
| Hydrogen .....        | 5 | .... | 5  | .... | 10.20  |
| Oxygen .....          | 1 | .... | 8  | .... | 16.33  |
| <hr/>                 |   |      |    |      |        |
| Oxide of allyle ..... | 1 |      | 49 |      | 160.00 |

The theory of the conversion of oil of mustard (sulphocyanide of allyle) into oil of garlic (sulphuret of allyle) by the action of potassium, as effected by Gerhardt, (*Comptes rendus*, Mars, 1845,) will now be apparent. In this case, cyanogen and sulphuret of potassium, (and not sulphocyanide of potassium) must be formed.  $C_6H_5NS_2 + K = C_6H_5S + K S + C_2N$ .

**OIL OF ASAFŒTIDA.** The peculiar and offensive odor of the gum-resin asafœtida appears to be derived from the presence of an essential oil, which may be obtained by distilling it with water, one-third of an ounce of the oil being the average produce from a pound of asafœtida: it is advisable to mix the gum-resin with pounded glass, or coarse sand, which prevents its adhesion to the bottom of the retort, and diminishes the violence of the concussions which are apt to ensue. The oil is yellow, its sp. gr. is 0.942. It has the concentrated odor of asafœtida, and tastes at first mild, and then acrid. It evaporates very rapidly, and soon fills a large room with its characteristic odor. It is very sparingly soluble in water, 1 part of the oil requiring about 2000 parts of water to dissolve it. It absorbs oxygen, and becomes resinous when exposed to air. It is a mixture of various oils, resolvable probably into two modifications, one of which is a compound of carbon, hydrogen, and oxygen; the other, of carbon, hydrogen, and sulphur. Dr. Stenhouse analyzed three portions of this oil obtained by separating the distillate at different temperatures, with the following results: (*Mem. Chem. Soc.*, i. 48.)



|               | I.<br>Boiling point 325°. |            | II.<br>Boiling-point 321°. |            | III.<br>Boiling-point 370°. |            |
|---------------|---------------------------|------------|----------------------------|------------|-----------------------------|------------|
| Carbon .....  | 66·16                     | .... 65·78 | 62·54                      | .... 62·60 | 58·42                       | .... 58·03 |
| Hydrogen .... | 9·83                      | .... 9·64  | 9·45                       | .... 9·05  | 9·12                        | .... 9·09  |
| Oxygen .....  | 1·08                      | .... 2·04  | 7·89                       | .... 8·36  | 15·58                       | .... 17·14 |
| Sulphur ..... | 22·93                     | .... 22·54 | 20·12                      | .... 19·99 | 16·88                       | .... 15·74 |
|               | 100·00                    | 100·00     | 100·00                     | 100·00     | 100·00                      | 100·00     |

The action of reagents on oil of asafœtida is as follows: nitric acid acts on it energetically, evolving nitric oxide, and converting it into a resin; and on adding a salt of baryta, there is an abundant precipitate of sulphate of baryta. Sulphuric acid first reddens, and then chars it. It readily dissolves iodine. It does not combine with ammonia. With salts of silver, lead, and mercury, it gives black precipitates. When brought into contact of peroxide of mercury, heat is evolved, and a greenish-yellow mass formed, which is not soluble in water. With corrosive sublimate it produces a white flocculent precipitate, insoluble in water, alcohol, and ether.

### § XIII. RESINS. GUM RESINS. BALSAMS. BITUMENS.

RESINOUS substances are very common in vegetables, and are found as proximate constituents of most plants; those which have been principally examined are such as either flow naturally from fissures in the bark or wood, or are obtained from incisions in the trees and shrubs which produce them. They are almost always in the first instance mixed with variable proportions of essential oil, which either evaporates on exposure to air, or becomes resinified by the action of oxygen. These mixtures of essential or volatile oil with resin are generally called *balsams*. The *gum resins* are natural mixtures of gum and resin, and the substances termed *bitumens* and *fossile* resins are probably of the same common origin, having been derived from antediluvian vegetables.

When pure, and free from all traces of essential oil, the *resins* are inodorous; but some of them emit characteristic odors when rubbed, and all of them when heated. A few of them are crystallizable. Their colors are generally derived from foreign substances, and when deprived of these, they are usually pale-yellow or brown; they are non-conductors of electricity, and become electric by friction. The greater number of them are heavier than, and insoluble in water; they have little taste, except when containing minute portions of other substances, which often confer upon them distinctive flavors. They are generally softened, or even fused, when boiled in water; and some of them, under such circumstances, form *hydrates*. In the air they burn with a sooty flame, and when subjected to dry distillation, yield volatile liquids and inflammable gases.

The natural resins are generally mixtures of two or more resinous substances, which may be more or less perfectly separated by the action of alcohol, in which the greater number of these bodies are soluble, more especially in absolute, or anhydrous alcohol; some of them, however, resist that solvent, even when aided by heat. They are also, for the

most part, soluble in ether, in sulphuret of carbon, and in the fat and volatile oils.

There are many of the resins which, when in alcoholic solution, redden litmus, and are soluble in, and even neutralize the alkalis; they therefore rank as *acids*: others are *indifferent*; and a few have been regarded as *basic*. The alcoholic solution of the acid resins is not precipitated by ammonia, and the precipitate which water occasions in it is entirely soluble in the aqueous solution of that alkali. On the other hand, the alcoholic solution of the indifferent resins is precipitated by ammonia. All the resins are thrown down from their solutions in alcohol by dilution with water, and they generally fall in a white, pulverulent, or curdy form, constituting what the old chemists termed a *magistery*. The acid resins are further distinguished by the crystalline precipitate which they occasion when their ammonio-alcoholic solutions are added to nitrate of silver. The compounds of the acid resins with the alkalis, forming *resinates*, or *resin-soaps*, are distinguished from the *oil-soaps* by neither forming a gelatinous emulsion when concentrated, nor being separable from water by the addition of common salt; but they are detergent, and lather like common soap.

Several of the resins are soluble without decomposition in cold sulphuric acid, and are precipitated unchanged when the solution is diluted: on the application of heat, sulphurous acid, and often carbonic acid, is evolved, water is formed, and a carbonaceous mass remains, which frequently contains artificial tannine. (HATCHETT, *Phil. Trans.*, 1805.)

Nitric acid also dissolves some of the resins, and if heat be applied, nitric oxide is evolved, and a variety of new products are obtained, depending upon the degree of concentration of the acid, its temperature, and the duration of its action. Acetic acid dissolves many of the resins, and is frequently a useful distinctive solvent.

It has been attempted to refer the resins to a common radical, and to consider them as definite oxides of definite hydrocarbons, but the results of their analysis do not as yet sanction such a generalization; it appears, however, from such of their combinations with metallic oxides as have been accurately examined, that the relation of the carbon to the oxygen in an atom, or equivalent of a resin, is never less than 40 atoms to 1, and that a great number of the resins admit of being represented by formulæ beginning with C<sub>40</sub>.

The *gum-resins* are extremely variable in composition, and many of them, in addition to their constituent gum and resin, contain volatile oils, separable from them by distillation with water, and conferring upon them characteristic odors. They are principally used in pharmacy. They are entirely soluble neither in alcohol nor in water, but when triturated with the latter, form milky mixtures resembling emulsions, in which the resinous particles are more or less permanently suspended by the dissolved gum.

The *balsams* have been already adverted to as mixtures of resins and volatile oils, and several of them contain peculiar acids, and other products, some of which have been above described, such as benzoic, cinnamic, succinic acid, &c. They are generally resolvable, by distillation with water, into volatile oils and resins, an instance of which is presented in the production of oil of turpentine already described.



*Bitumens* are of different degrees of consistence, and in some respects analogous to balsams, affording, when distilled, either *per se*, or with water, certain volatile hydrocarbons or naphthas, and oxyhydrocarbons, and leaving resinoid substances, or *retinasphalts*, and *asphalts*.

Lastly, there are substances partaking, in certain of their properties, of the character of resins, but peculiar in composition and in chemical and physical properties, namely, the varieties of *caoutchouc* and *gutta percha*; they are afforded by several plants, and have their antediluvian congener in *elastic bitumen*.

## RESINS.

**COLOPHONY.**  $C_{40}H_{30}O_4$ . *Common Rosin*. This is the residue, above adverted to, of the distillation of common *terpentine*; it retains more or less water, and is known as *white* and *yellow resin*, being in this state translucent, and often slightly viscid. When deprived of water, by fusion, it is termed *brown*, or *black resin*, *colophony*, *rosin*, or *fiddlers' rosin*.

Rosin is a brittle, tasteless, and almost inodorous substance, of a smooth shining fracture; its sp. gr. is 1.080. It softens at  $160^{\circ}$  to  $170^{\circ}$ , but does not enter into fusion under  $275^{\circ}$ . According to the analysis of Blanchet and Sell, this substance, in its pure state, may be represented as composed of  $C_{40}H_{30}O_4$ , (*Ann. der Pharm.*, vi. 259;) but Unverdorben has shown, that colophony includes two distinct acid resins, together with a minute portion of an indifferent resin. (*Poggend. Ann.*, xi. 47.) These acid resins he designates *pinic acid*, and *silvic acid*, the former greatly preponderating. As respects the composition of these acids, it appears that they are *isomeric*, and therefore have the same formula as that above ascribed to pure colophony, a conclusion sanctioned by the analyses of Rose, (*Poggend. Ann.*, xxxiii. 42, and liii. 265;) of Trommsdorff, (*Ann. der Pharm.*, xiii. 169,) and of Laurent, (*Ann. Ch. et Ph.*, lxxv. 324,) but apparently not sanctioned by Löwig. (*Chem. der Org. verbind.*, ii. 1101.)

*Silvic Acid.*  $C_{40}H_{30}O_4$ . (*Resin beta of colophony*. BERZELIUS.) This substance is obtained,—1. By mixing an alcoholic solution of colophony with an alcoholic solution of oxide of copper, drying the precipitate, and digesting it in absolute alcohol, which dissolves the silvate, but leaves the pinate of copper. Sulphuric acid is added to the alcoholic solution, and it is then precipitated by water, which throws down silvic acid, and which, dissolved in alcohol, yields crystals on evaporation. (UNVERDORBEN.) 2. Colophony is digested in cold alcohol; the insoluble portion is then dissolved in two parts of boiling alcohol, of sp. gr. 0.863. On cooling, it deposits the silvic acid, which must be redissolved in alcohol, and purified by crystallization. (TROMMSDORFF.) Further details respecting the preparation and purification of this substance are given by Trommsdorff and by Löwig.

Silvic acid forms tabular and prismatic crystals, easily soluble in absolute alcohol, and in ether. The alcoholic solution reddens litmus, and is decomposed by water, which throws down a glutinous precipitate obstinately retentive of alcohol. It dissolves in fat and volatile oils, and in naphtha, but cannot be obtained crystalline from these solvents.

The crystallized acid fuses at  $285^{\circ}$ , and concretes, on cooling, into a transparent vitreous mass, which fuses between  $195^{\circ}$  and  $230^{\circ}$ . The amorphous acid may again be crystallized from its solution in alcohol. (WÖHLER.) The components of the *crystallized* acid are

|             |    |      |     |      |        | Rose. |        | Trommsdorff. |         | Laurent. |        |
|-------------|----|------|-----|------|--------|-------|--------|--------------|---------|----------|--------|
| Carbon..... | 40 | .... | 240 | .... | 79.47  | ....  | 79.28  | ....         | 79.659  | ....     | 79.50  |
| Hydrogen    | 30 | .... | 30  | .... | 9.93   | ....  | 9.95   | ....         | 9.818   | ....     | 9.90   |
| Oxygen .... | 4  | .... | 32  | .... | 10.60  | ....  | 10.77  | ....         | 10.523  | ....     | 10.60  |
| <hr/>       |    |      |     |      |        |       |        |              |         |          |        |
| Silvic acid | 1  |      | 302 |      | 100.00 |       | 100.00 |              | 100.000 |          | 100.00 |

The *salts of the silvic acid* have been principally examined by Unverdorben, and by Rose. Those with an alkaline base are formed, according to Unverdorben, by digesting their carbonates in an ethereal solution of the acid; carbonic acid is evolved, and the resulting silvate is dissolved by the ether, from which it may be obtained by evaporation. When an aqueous solution of a salt of the earths, or other metallic oxides, is dropped into an alcoholic solution of silvate of potassa, the silvate of the earth or oxide is precipitated. *Silvate of Potassa* resembles a colorless resin, and is soluble in all proportions in water: if pure, or carbonated potassa, or an alkaline salt, be added to the aqueous solution, it passes into *oxysilvate of Potassa*, but the alcoholic and ethereal solutions of silvate of potassa are not thus altered. This salt is insoluble in oil of turpentine and in olive oil. When its hot alcoholic solution is mixed with a similar solution of the pure acid, soft acicular crystals of an *acid silvate* are deposited on cooling. The combinations of silvic acid with the *alkaline earths* are insoluble in water, but soluble in 6 parts of cold anhydrous alcohol. *Silvate of Magnesia* is soluble, in all proportions, both in anhydrous alcohol, and in alcohol of sp. gr. 0.865; a property which is said to distinguish it from pinate of magnesia. The *Silvates of Manganese* and of *Zinc* are white, pulverulent, infusible at  $212^{\circ}$ , insoluble in alcohol, but soluble in ether, oil of turpentine, and olive oil. *Silvate of Copper* is a green powder, very sparingly soluble in alcohol, but abundantly in ether and in oils. *Silvate of Lead* is a white crystalline precipitate, formed by mixing alcoholic solutions of silvic acid and acetate of lead; it softens at  $212^{\circ}$ , and is soluble in ether; it consists of

|                      |   |     |     |     |        | Rose. |        |
|----------------------|---|-----|-----|-----|--------|-------|--------|
| Oxide of lead .....  | 1 | ... | 112 | ... | 27.05  | ...   | 27.03  |
| Silvic acid .....    | 1 | ... | 302 | ... | 72.95  | ...   | 72.97  |
| <hr/>                |   |     |     |     |        |       |        |
| Silvate of lead..... | 1 |     | 414 |     | 100.00 |       | 100.00 |

*Silvate of Silver.* No precipitate ensues on mixing an alcoholic solution of nitrate of silver with an alcoholic solution of silvic acid; but on adding ammonia to the mixture, a crystalline precipitate falls, soluble in ether, and somewhat soluble in alcohol, composed of

|                         |   |     |     |     |        |        |
|-------------------------|---|-----|-----|-----|--------|--------|
|                         |   |     |     |     |        | Rose.  |
| Oxide of silver .....   | 1 | ... | 116 | ... | 27.75  | 27.95  |
| Silvic acid .....       | 1 | ... | 302 | ... | 72.25  | 72.05  |
| <hr/>                   |   |     |     |     |        |        |
| Silvate of silver ..... | 1 |     | 418 |     | 100.00 | 100.00 |

*Oxysilvic Acid.*  $C_{40}H_{29}O_7$ . *Amorphous silvic acid.* (ROSE.) When the alcoholic solution of silvic acid is left for some weeks exposed to the



air, it is no longer crystallizable, but on evaporation *in vacuo* over sulphuric acid, leaves a viscid mass, which, when fused in a water-bath, loses from 4 to 7 *per cent.* in weight, and acquires the appearance of pure colophony. The same resinous substance remains when the alcoholic solution of silvic acid is left to slow spontaneous evaporation in the air. This white, brittle, resinous product, when dried upon a water-bath, consists of  $C_{40} H_{29} O_7$ .



*Pinic Acid.* (*Resin alpha of colophony.* BERZELIUS.) When pinate of copper, obtained as above described (p. 1572), is dissolved in boiling alcohol acidulated by hydrochloric acid, and water added to the mixture, pinic acid is precipitated, in the form of a colorless resin, provided colorless colophony had been used in its preparation. This substance is soluble in alcohol, ether, oil of turpentine, and naphtha, and is not susceptible of crystallization. In all other respects it resembles silvic acid and colophony. The *pinates* are said to be less soluble in ether than the *silvates*, and *pinate of magnesia* is represented as insoluble in alcohol, whereas the *silvate* is soluble.

*Colopholic Acid.* (*Resin gamma of colophony.* BERZELIUS.) This term is applied by Unverdorben to the product formed by heating silvic or pinic acid, or colophony, somewhat above its point of fusion; it becomes brown, and its acid character is increased; when pinic acid is fused, and boiled down to one-fourth of its original bulk, the residue is almost entirely colopholic acid. It is represented as scarcely soluble in alcohol of sp. gr. 0.875; but its combinations appear to resemble the *silvates* and *pinates*. When colophony is rapidly distilled over an open fire, it is resolved into carbon, water, and *colophene* (p. 1540); there is also formed a liquid hydrocarbon  $= C_{10} H_8$ , having the properties of *terebene* (p. 1540). (DEVILLE.) But these products probably vary with the mode of distillation, for Fremy represents them as consisting of water, together with a thick yellow oil, which he terms *resinéine*, and represents as  $= C_{40} H_{28} O_2$ ; and by distilling in the same way, a mixture of 1 part of resin and 8 of powdered quick-lime, he obtained two liquids, which he calls *resinone*  $= C_{10} H_9 O$ , and *resinéone*  $= C_{29} H_{23} O$ ; carbonic acid being at the same time formed. (*Ann. Ch. et Ph.*, Lix. 5.)

*Pimaric Acid.*  $C_{40} H_{30} O_4$ . Under this name Laurent (*Ann. Ch. et Ph.*, LXXii. 383) has described the resin of the turpentine of *Pinus maritima*; the trees grow in the plains of Bordeaux; the barks are wounded, and the turpentine which exudes collects partly in holes dug at the foot of the tree, and partly concretes upon the trunk, forming large white masses of a softish consistence, which are separately collected, and known under the name of *galipot*; they are principally composed of granular crystals of *pimaric acid*, to obtain which, the whitest and cleanest masses are selected, wiped, and broken into fragments of the size of a pea; they are then covered with a mixture of 6 parts of alcohol and 1 of ether, well stirred, and broken down with a glass rod; the liquor is then decanted, and the residue dissolved in boiling alcohol; this solution deposits, in the course of two or three days, a crust which gradually increases in thickness, and which must be removed before the deposition is quite complete, washed with alcohol, and redissolved in boiling



alcohol; on cooling, and by spontaneous evaporation, pure pimaric acid is deposited; the alcoholic mother-liquors also yield a further portion, in the form of a white crystalline powder, composed of microscopic prisms. The acid may also be obtained, in the same way, from the colophony of Bordeaux.

Pure pimaric acid forms a white crystalline mass, very soluble in ether: alcohol, at the temperature of  $65^{\circ}$ , dissolves about one-tenth of its weight: boiling alcohol dissolves about its own weight. When the alcoholic solution is poured into a large quantity of water, a flocculent precipitate falls, which, when separated upon a filter, and dried in the air, is pulverulent, and not agglutinated. Pimaric acid fuses at about  $260^{\circ}$ , but does not afterwards again harden till cooled down to  $158^{\circ}$ . If rapidly fused in a platinum capsule, and withdrawn from the heat as soon as liquid, it concretes into a beautifully limpid resin, resembling rock crystal; by prolonged fusion it acquires a yellow, and then a brown tint.

The *Pimarales of Ammonia, Potassa, and Soda* are soluble in water and in alcohol. The alcoholic solution of the acid produces no precipitate in the chlorides of calcium, barium, strontium, or magnesium, nor does it give any immediate precipitate in alcoholic solutions of acetate of copper, lead, or silver; but, after a time, the liquors become turbid, and uncrystallizable bisalts are deposited. The *Bipimarales of Lead* is white, and fuses like a resin.

The composition of pimaric acid is precisely that of silvic and pinic acid.

When pimaric acid is distilled *in vacuo*, a liquid rises, which concretes in the neck of the retort, and appears to be unchanged acid; but if it be dissolved in alcohol, and left to spontaneous evaporation, it now forms tabular, or lamellar crystals, of a triangular form. This modification of the acid, called by Laurent *pyromaric acid*, may also be obtained by distillation under ordinary atmospheric pressure, but in that case a portion of oil is at the same time formed. It admits of repeated distillations, with little further change.

*Pyromaric acid* is easily distinguished from pimaric acid, by pouring a dilute solution of it in boiling alcohol into a very concentrated boiling alcoholic solution of acetate of lead; no immediate precipitation ensues, but after a time, long prismatic acicular crystals are formed. This acid has the same composition and equivalent as the pimaric acid, of which it must be regarded merely as a molecular modification.

When a solution of pimaric acid in cold sulphuric acid is poured into water, a flocculent precipitate of a slightly red tint falls, which when washed becomes almost colorless, but when dried, and dissolved in alcohol, does not crystallize: it is a *hydrated pimaric acid*, containing 2 atoms of the acid with 1 of water.

When pimaric acid is boiled in nitric acid, nitrous fumes escape, and a yellow resinous substance collects upon the surface, which, when purified, is insoluble in water, very soluble in alcohol and in ether, and not crystallizable. This substance, called by Laurent *azomaric acid*, is represented by the formula  $C_{20}H_9O_6N + 2HO$ ; (deduced from the analysis of its combination with oxide of lead).

The oily matter, small quantities of which are produced (along with



a portion of water and pyromaric acid), when pimaric acid is subjected to dry distillation, and which has been named *pimarone*, has the formula  $C_{20} H_{14} O$ .

ELEMI is "a concrete resinous exudation from one or more unascertained plants." There are several varieties of it, one of which appears, according to Pereira, to be the produce of the *Canarium balsamiferum* of Ceylon; and another, of the *Icica Icicariba* of the Brazils. Elemi is at first soft, and somewhat viscid, but becomes hard and brittle by cold and by age; it is yellow, translucent, and of a peculiar odor, somewhat resembling fennel; it yields a volatile oil when distilled with water (p. 1543). Elemi contains about 60 parts of an *acid resin*, soluble in cold alcohol, and 20 parts *per cent.* of an indifferent crystallizable resin, soluble in hot alcohol. The latter has been analysed by Hess (*Poggend. Ann.*, xLvi. 319), by Rose (*ibid.* xLviii. 61), and by Marchand (*Erdmann and Marchand's Journ.*, xviii. 322). They represent it as  $= C_{40} H_{33} O$ . According to Rose, a solution of the crystalline resin in alcohol, left to spontaneous evaporation, is partly converted into an amorphous resin, in consequence of combination with water. According to Johnston, the portion of elemi soluble in cold alcohol (resin  $\alpha$ ), is  $= C_{40} H_{32} O_4$ , while the other portion (resin  $\beta$ ) is  $= C_{40} H_{33} O$ .

ANIME. This resin is the produce of *Hymenæa Courbaril*, a tree growing in Brazil; it consists, like elemi, of two resins: one, soluble in cold alcohol; and the other, crystallizable from its hot alcoholic solution; the latter has been analyzed by Laurent (*Ann. Ch. et Ph.*, Lxvi. 314), who assigns to it the formula  $C_{40} H_{33} O$ , or  $C_{40} H_{32} + HO$ .

SANDARACH (*Juniper resin*) is the produce of *Thuia articulata*, which grows in Barbary: it is imported from Mogadore, and largely used as an ingredient in varnishes. It usually occurs in small, yellow, brittle drops, easily fusible, and soluble in alcohol. According to Unverdorben and Johnston, it is separable into three resins. Resin  $\alpha$  is soluble in hot alcohol, and of comparatively difficult fusion,  $= C_{40} H_{30} O_6$ . Resin  $\beta$ , difficultly soluble in alcohol, and also difficultly fusible,  $= C_{40} H_{31} O_5$ . Resin  $\gamma$ , soluble in cold alcohol, and becoming soft at  $212^\circ$ , constitutes three-fourths of ordinary sandarach.

MASTIC is the produce of the *Pistacia Lentiscus*, native in the south of Europe, the north of Africa, and the Levant, particularly the island of Chios; it occurs in small spheroidical, translucent tears, of a pale yellow color, vitreous fracture, agreeable odor, and mild aromatic taste. When chewed it becomes tough and somewhat viscid. It fuses at about  $250^\circ$ , and begins to be decomposed: it contains a very minute quantity of volatile oil, and about 90 *per cent.* of a resin easily soluble in alcohol (*masticic acid*)  $= C_{40} H_{31} O_4$ , and of a viscid and difficultly soluble resin (*masticine*)  $= C_{40} H_{31} O_2$ . (JOHNSTON, *Phil. Trans.*, 1840.) Mastic is a valuable ingredient in certain varnishes, and is frequently used for the purpose of stopping decayed teeth.

BOTANY BAY RESIN, said to be the produce of *Acarois resinifera*, is

of a yellow color, brittle, and of a slightly astringent taste. It exhales a fragrant odor when heated, and dissolves in alcohol and ether. It resembles tolu balsam in containing cinnamic acid, and a small quantity of benzoic acid. (LICHTENSTEIN, *Crell's Annals*, 1799, ii. 242. STENHOUSE, *Mem. Chem. Soc.*, iii. 10.)

**BENZOIN.** This substance has already been alluded to as the source of *benzoic acid*. The finer kinds are frequently called *Siam benzoin*, the coarser and less pure kind is termed *Calcutta benzoin*. It is generally met with in masses composed of white translucent tears, apparently connected together by a brown transparent resin, presenting an amygdaloid appearance, which in the coarser kinds is much less distinct. It has been repeatedly examined, but most recently by Schrötter (*Poggend. Ann.*, lix. 72), and by Johnston. Unverdorben has announced in it the presence of three distinct resins: 1. (resin  $\alpha$ ) soluble in ether, but insoluble in solution of carbonate of potassa; 2. (resin  $\beta$ ) insoluble both in ether and in carbonate of potassa; 3. (resin  $\gamma$ ) soluble in ether and in carbonate of potassa. An extended abstract of the chemistry of the resins of benzoin will be found in Löwig. (*Chem. d. Org. verbind.*, ii. 1138. See also JOHNSTON, "On the constitution of the Resins," *Phil. Trans.*, 1840, p. 383.)

**GUAIAIACUM.** This substance is the produce of the *Guaiacum officinale*, a lofty tree, native in St. Domingo and Jamaica. It occurs in tears, naturally exuding from the stem; and in lumps, obtained partly from incisions into the trunk of the tree, and partly by the action of heat upon billets of the wood. This resin is of a dark, dingy-green color, transparent when in thin laminae, and of a brilliant, resinous fracture. It has a slight balsamic odor. Its powder is at first pale grey, but gradually deepens, and becomes green by exposure; it acquires a beautiful but transient blue color, when moistened with spirit of nitrous ether. According to the *Edinburgh Pharmacopœia*, the characters of guaiacum resin are as follow: "Fresh fracture red, slowly passing to green; the tincture slowly strikes a lively blue color on the inner surface of the paring of a raw potato." The sp. gr. of guaiacum varies between 1.20 and 1.23. It is soluble, to the extent of about 90 *per cent.*, in absolute alcohol. The insoluble portion, though sometimes described as resin, has more of the characters of altered extractive. When subjected to dry distillation, guaiacum fuses at about 570°, and an oily matter, together with water, passes over, which has been examined by Sobrero, (*Ann. der Pharm.*, xxx. 19,) and by Pelletier and Walter. (*Erdmann and Marchand's Journ.*, xxxiii. 316.) It has been termed *Guaiacole*, and the formula assigned to it is C<sub>14</sub> H<sub>8</sub> O<sub>4</sub>.

When finely-powdered guaiacum is exposed to the air, it slowly absorbs oxygen, and acquires a deep green color; and a piece of paper dipped into tincture of guaiacum, and exposed in the prismatic spectrum, undergoes this change of tint most rapidly in the violet ray, whilst in the red ray, the green color is destroyed. Chlorine, and aqueous solution of chlorine, render guaiacum first green, then blue, and lastly brown, and by the cautious addition of a solution of chlorine to tincture of guaiacum, these changes of color, with a variety of intermediate tints, may be well



observed. When guaiacum has been rendered brown by chlorine, it reverts to green by the action of ammonia, and dissolves in caustic ammonia with a deep green color. Digested with nitric acid, guaiacum is rendered green, blue, and brown, and ultimately dissolves: the alkalis occasion a brown precipitate in this solution when recently prepared. With sulphuric acid guaiacum forms a brown solution, which, on dilution with water, gives a lilac-colored precipitate. It is readily soluble in caustic potassa and soda, forming compounds which have been called *guaiacates*, by those who designate the resin *guaiacic acid*. The most beautiful tints of green and blue may be obtained by dropping different proportions of an alcoholic solution of guaiacum into spirit of nitrous ether, and precipitates of various colors may be then thrown down by the addition of water; these changes of color, setting out with green, and passing through various shades of blue and brown, appear to indicate different states of oxidizement of the resin. (BRANDE, *Phil. Trans.*, 1806.) The gluten of wheat, and not the starch, is said to change guaiacum to blue, so that it has been proposed as a test of the goodness of wheaten flour. Milk, and different roots, possess the same property. According to Johnston, guaiacum may be represented as  $C_{40}H_{23}O_{10}$ . Pagenstecher has proposed tincture of guaiacum as a test of the presence of hydrocyanic acid, (*Quart. Journ. of Science*, &c., x. 182,) and if the tincture be added to a very weak aqueous solution of that acid, and afterwards a few drops of a solution of sulphate of copper, a blue color ensues, which is rendered more intense by the addition of alcohol; but, as so many substances render guaiacum blue, the test is not sufficiently characteristic to be useful.

RESIN OF JALAP is obtained from the *jalap* of commerce, which, according to Pereira, is the root of *Ipomœa purga* (*Ipomœa jalapa*) and not of *Convolvulus jalapa*, as frequently stated. The plant grows in the woods of the Mexican Empire, near Chicanguico, and Jalapa is the only market for the root, whence it is exported to Europe by way of Vera Cruz. Resin of jalap is extracted by alcohol from the pulverized root, the tincture is precipitated by dilution with water, and the precipitate washed, dried, and redissolved in alcohol, from which it is obtained by evaporation.

It has a bitterish acrid taste, and a peculiar odor; it is very soluble in alcohol, but less so in ether. Triturated with milk, it does not form an emulsion, but its particles unite into a solid mass; it is said that this property distinguishes it from scammony resin. According to Buchner and Herberger, jalap-resin consists of a *basic resin* (*jalapine*) and an *acid resin* (*jalapic acid*). According to Kayser (*Ann. der Pharm.*, lix. 81), jalap resin may be resolved by ether into a resin soluble in that liquid, and one which is insoluble. The *soluble resin* (resin *a*) is obtained by digesting purified resin of jalap in ether, and evaporating; it remains in the form of a soft brown substance. When dissolved in alcohol and precipitated by water, it is a soft resinous brown substance, reddens litmus, has an acrid taste, and a strong jalap odor. It does not harden by exposure to air. If left for some months covered with water, it becomes converted into an adherent mass of prismatic crystals. It is insoluble in acids, but very soluble in the alkalis, and the acids precipi-

tate its alkaline solutions. Its alcoholic solution occasions a yellow precipitate in an alcoholic solution of acetate of lead. The portion of jalap resin which is *insoluble* in ether (resin  $\beta$ ), and which is identical with *jalapine*, furnishes a beautiful red liquor when dissolved in sulphuric acid, and has therefore been called, by Kayser, *rhodeoretine*: its composition is  $C_{42}H_{35}O_{20}$ . When purified, it is nearly white, pulverulent, inodorous, tasteless, insoluble in water and in ether, but very soluble in alcohol. When its alcoholic solution is mixed with water, a white precipitate falls, soluble in ammonia, and in acetic acid. It fuses at  $300^{\circ}$ , without loss of weight, into a pale yellow transparent substance. When rhodeoretine is dissolved in hot solution of carbonate of potassa, and evaporated to dryness on a water-bath, alcohol digested upon the residue dissolves *rhodeoretinate of potassa*, which may be obtained by distilling off the alcohol. In this combination, the rhodeoretine has passed into *hydrorhodeoretine*; that is, it has united to an atom of water, and is now  $C_{42}H_{36}O_{21}$ . Its combinations with several other bases have been described and analysed by Kayser. A form of jalap resin for pharmaceutical purposes has been suggested by Nativelle (*Journ. de Pharm. et de Chim.*, i. 228), prepared as follows: The sliced root is softened by the affusion of boiling water, and pressed out; and this treatment is repeated till the expressed water is colorless; the root, thus deprived of coloring matter by water, is then extracted by boiling alcohol, and when every thing soluble has been thus taken up, the different tinctures are mixed, agitated with a little animal charcoal, filtered, and distilled in a water-bath. The residue is then dried, and is white, friable, and energetically purgative.

**SCAMMONY RESIN.** The substance known in pharmacy under the name of *scammony*, is an exudation from incision of the root of the *Convolvulus scammonia*, and appears first as a milky juice, which afterwards dries. It is often very considerably adulterated. Several varieties of this drug come into the market, but the most select is imported from Smyrna, and occasionally from Trieste, under the name of *Virgin* or *Lachryma scammony*. It is of a dark greenish-gray color, moderately hard, and of a somewhat resinous fracture. It should not effervesce with hydrochloric acid, nor should its cold filtered decoction be blued by iodine. 100 grains, when incinerated with nitrate of ammonia, should not yield more than about 3 grains of ashes: ether should abstract from it at least 78 *per cent.* of resinous matter. (PEREIRA, *Mat. Med.*, p. 1264.) The odor of scammony, especially when breathed upon or moistened, is peculiar, and when a little water is rubbed upon its surface it should easily lactify.

The *resin of scammony*, obtained by evaporating its ethereal solution, is transparent, and of a brown tint, but may be decolorized by animal charcoal. Its alcoholic solution is feebly acid, and water throws down from it the resin in the state of *hydrate*. According to Johnston, it is remarkable as containing more oxygen than any other resin hitherto analysed, its formula being  $C_{40}H_{33}O_{20}$ . It is a powerful cathartic. (*Phil. Trans.*, 1840, p. 341.)

**DRAGON'S BLOOD.** This is a deep red resin imported from the East



Indies. The finest kind is in large red drops, or tears, and is said to be the produce of *Calamus draco*. It also occurs in masses of various degrees of purity, and in sticks enveloped in palm leaves, but these varieties appear to be more or less adulterated. Pure dragon's blood is of a deep red color, soluble in alcohol and ether, and in alkaline solutions. It has many characters in common with the coloring resin of *red saunders*, the wood of *Pterocarpus santalinus*, (p. 1508.) It appears to be susceptible of combination with metallic oxides, forming red compounds. Herberger applies the term *draconine* to the purified resin. When subjected to dry distillation, it first fuses, and then yields water, acetone, and about 3 per cent. of benzoic acid; as the temperature rises, carbonic oxide and carbonic acid are formed, and an oily product, containing a hydrocarbon isomeric with *toline*, and termed by Glénard and Boudault (*Journ. de Pharm. et Chim.*, vi. 205), *dracyle* =  $C_{14}H_8$ . (See also *toline*, as described by Muspratt and Hofmann. *Mem. Chem. Soc.*, ii. 367.)

DAMMARA RESIN is a white resin brought from the East Indies, and is said to be the produce of the *Pinus dammara*: it contains a resin soluble in alcohol (*resin α*), and one insoluble in alcohol (*resin β*). It has been examined by Brandes, Lucanus, and Thomson. (BERZELIUS, *Lehrbuch*; THOMSON, *Ann. der Pharm.*, xlvii. 351; *Thomson's Org. Chem.*, p. 539.)

COPAL. This resin is highly important as an ingredient in certain varnishes; it is produced in India, and in the West Indies, and America. The *hard copal* is said to be the produce of the *Hymenæa verrucosa*; it is generally in large hard pieces, of a slightly yellow tint, a conchoidal fracture, transparent, and often includes insects and vegetable remains; it is inodorous and tasteless. Its sp. gr. varies between 1.045 and 1.139. When heated, it softens without acquiring viscosity, and at a higher temperature fuses, suffering partial decomposition, and exhaling a peculiar aromatic odor. When boiled in alcohol, a small portion only dissolves, and the residue swells and softens: it is said, however, that when moistened, and long exposed to air, it gradually absorbs oxygen, and acquires more of the common resinous characters. Among the essential oils, oil of rosemary is said to be one of the best solvents of copal, and to take up more than oil of turpentine. According to Unverdorben (*Thomson's Org. Chem.*, 546), and Filhol (*Journ. de Pharm. et Chim.*, i. 316 and 401), no less than five modifications of resin are contained in copal (from Calcutta), four of which are separable by the action of ether, alcohol, and alkaline solutions, while a fifth remains insoluble in those agents.

According to Messrs. Soehnée, as quoted by Dumas, copal, which has first been reduced to an impalpable powder, and then exposed for at least twelve months to the air, acquires solubility in alcohol, and may in that state be used for the preparation of a number of varnishes. In the same way, *shell-lac* (p. 1510), acquires easy solubility in alcohol after protracted exposure to air. When copal has been fused, and especially if set fire to, and allowed to burn for some minutes, it is so far altered as to become more soluble in alcohol, but its quality is deteriorated, so that the varnishes which it then affords are no longer hard and brilliant; nor is much

advantage attained by fusing copal with turpentine, or with other readily soluble resins.

Dumas, Ure, and Aikin, have given a variety of receipts for copal, and other varnishes. (*Chim. app. aux Arts*, vii. 348; *Ure's Dict. of Arts*; and *Aikin's Chemical Dictionary*, Art. VARNISH.)

According to Dumas, the principal substances used in varnishes are the following:

| Solvents.       |  | Solids.   |            | Colors.         |               |
|-----------------|--|-----------|------------|-----------------|---------------|
| Oil of Nuts.    |  | Amber.    | Elemi.     | Gamboge.        | Annotta.      |
| „ Linseed.      |  | Copal.    | Benzoin.   | Dragon's blood. | Red Saunders. |
| „ Turpentine.   |  | Mastic.   | Colophony. | Aloes.          | Cochineal.    |
| „ Rosemary.     |  | Sandarac. | Arcanson.  | Saffron.        | Indigo.       |
| Alcohol. Ether. |  | Lac.      | Anime.     | Turmeric.       |               |

Several other substances are however occasionally employed in the preparation of varnishes: asphaltum, for instance, is an ingredient in *Japan* or *black varnish*, and caoutchouc in those which are required to be elastic and waterproof. The characters of a good varnish are, that it should retain brilliancy, and neither appear dull nor greasy; that it should firmly adhere to the surface to which it is applied, and neither crack nor scale off; that it should not change color, or lose lustre, in consequence of exposure to light and air; and that it should not be a very long time in drying. Varnishes are generally distinguished as *spirit* and *oil varnishes*; the former are generally the most brilliant, but also most brittle; the toughest and best spirit varnishes being those containing lac or copal. The article known under the name of *French polish*, is an alcoholic solution of shell-lac; and a small quantity of oil is generally added at the time of its application; it is laid on by a ball of cotton-wool, and then rapidly rubbed in the direction of the fibres of the wood: it is ultimately finished off, after drying, by friction with tripoli and oil. The varnishes prepared with oil of turpentine are generally less brittle than those in which only alcohol is used, inasmuch as the turpentine itself dries into a soft resin.

## GUM-RESINS.

**AMMONIACUM.** This term has been applied to two different gum-resins; the one the produce of *Ferula tingitana*; the other, of *Dorema ammoniacum*; the latter is the commercial ammoniacum of the present day. The plant is a native of Persia; it is pervaded with a milky juice, which oozes forth upon the slightest puncture, and hardens into ammoniacum. It does not appear that artificial incisions are ever made in the stem; but when the plant has attained perfection, innumerable beetles, armed with an anterior and posterior probe of half an inch in length, pierce it in all directions; the ammoniacum soon oozes and concretes, and is then picked off, and sent, *viâ* Bushire, to India and various parts of the world. It is usually imported into England from Bombay, but occasionally comes from the Levant. (PEREIRA, *Mat. Med.*)

Ammoniacum occurs in tears or drops, and in masses composed of agglutinated tears; it has a faint and somewhat unpleasant, but very peculiar odor, best detected by heating it; it has a bitter nauseous taste;



the tears are brown exteriorly, but pale buff, or nearly white within; and nearly opaque. At ordinary temperatures, ammoniacum is hard and tough, but softens like wax in the hand; it may be pulverised in frosty weather. According to Braconnot's analysis (*Ann. de Chim.*, LXVIII. 69), it contains about 70 *per cent.* of resin, and 18 of gum: it also contains a glutinous matter, insoluble in water and alcohol (caoutchouc?), and an essential oil, transparent, and lighter than water. According to Johnston, the elements of the *resin* of ammoniacum, after drying at  $212^{\circ}$ , are  $C_{40} H_{25} O_9$ . (*Phil. Trans.*, 1840, p. 350.)

**ASAFŒTIDA.** This gum resin is obtained by making incisions into the upper part of the root of the *Ferula asafœtida*, a plant growing in Persia. It occurs in masses of a reddish and brown color, often made up of agglutinated tears. Its strong, alliaceous, and peculiar odor is well known. Exposed to light and air, its recently broken surface soon acquires a red color, which gradually passes into yellowish or pinkish brown; its taste is acrid and bitter. It contains variable proportions of gum and resin, together with a volatile oil already noticed. (p. 1569.) The resin of asafœtida has been examined by Johnston: it is very sensible to the action of light, which gradually renders it purple. Johnston assigns to it the formula  $C_{40} H_{26} O_{10}$ , and observes that it differs from ammoniac-resin in containing the elements of an additional atom of water: he failed in detecting sulphur in it. (See p. 1569.)

**BDELLIUM.** This term is applied to two gum-resins; one of these is *Indian bdellium*, or *false myrrh* (the *bdellium* of Scripture), and is obtained from *Amyris commiphora*: the other, or *African bdellium*, is the produce of *Heudolotia Africana*, a native of Senegal, and called by the natives, who make toothpicks of its spines, *niottout*; it consists of oval tears, of a brownish-yellow color, a feeble peculiar odor, and bitter taste. Pelletier (*Ann. de Chim.*, LXXX. 39) found it to consist of resin 60, gum 40, with a trace of volatile oil. The *resin* of bdellium, analyzed by Johnston, agrees with the formula  $C_{40} H_{31} O_5$ .

**EUPHORBIIUM** is the produce of different species of *euphorbia*, a plant growing in the interior of Africa; it exudes in the form of a milky juice, so acrid as to excoriate the fingers, and which hardens by the heat of the sun into irregular yellowish tears. It is nearly inodorous, but its dust excites incessant sneezing; its taste, at first slight, is afterwards acrid and burning; when swallowed, it produces vomiting and purging, and acts as an acrid poison; the persons who grind it suffer from headache and giddiness, and often from delirium. It consists principally of resin, and a waxy matter, and contains a considerable quantity of malate of lime. According to Rose (*Poggend. Ann.*, LIII. 369), euphorbium contains two distinct resins; one, easily soluble in cold alcohol; the other, only soluble in hot alcohol, and under certain circumstances susceptible of crystallization. These resins have also been examined by Johnston, but there is some doubt as to the results of the analysis. Rose assigns the formula  $C_{40} H_{35} O_4$ , to the crystallizable resin. Euphorbium has also been examined by Buchner and Herberger, who regard one of the resins as basic, the other acid. (*Buchner's Repertorium*, xxxvii.)

**GALBANUM.** This gum-resin is stated to be the produce of an umbelliferous plant, called by Don, *Galbanum officinale*; it is imported from the Levant, and from India, but the precise country where it is produced has not been ascertained; it generally occurs in masses of a brownish-yellow color, apparently composed of agglutinated tears; it has a peculiar odor, and a hot and bitter taste. It has been examined by Pelletier, and by Meissner, and its resin has been analysed by Johnston; it contains about 60 *per cent.* of resin and 20 of gum, and yields, when distilled with water, a volatile oil, colorless and limpid, and of a camphor-like odor. The formula assigned to the resin is  $C_{40}H_{27}O_7$ .

**GAMBOGE.** This gum-resin, which forms a well-known yellow water-color, is said to be the produce of the *Hebradendron cambogioides*, a native of Ceylon, and to drop from the broken leaves and branchlets in the form of a yellow milky juice (whence the term *gummi guttæ*). It is sometimes run into bamboos, so as to form cylindrical sticks; in other cases it is suffered to harden in masses, which are enveloped with leaves. The finest gamboge is brittle and inodorous, and at first has little taste, but afterwards occasions an acrid sensation in the throat: its fracture is conchoidal, and its fractured surface opaque, orange-colored or reddish-yellow, and smooth and somewhat glistening. Its powder is bright yellow. It forms a yellow emulsion with water, the films of which are good microscopic objects for observing the *active molecules* described by R. Brown. (*Phil. Mag.*, Sept., 1828.) Gamboge may be resolved into resin and gum, by the successive action of ether and water. The finest gamboge contains about 70 *per cent.* of resin, which is of a deep orange color, and communicates a yellow tint to 10,000 times its weight of alcohol. Its formula, according to Johnston, is  $C_{40}H_{23}O_8$ . When heated to about  $400^{\circ}$ , it undergoes partial decomposition, a resin soluble in cold alcohol being formed, and another, insoluble in that liquid; the latter is  $C_{40}H_{22}O_9$ . Gamboge resin (termed by Johnston, *gambodic acid*) forms numerous salts. (*Phil. Trans.*, 1839, p. 299.) Gamboge is a drastic purgative, resembling euphorbium in its virulence, and generally occasioning nausea and vomiting.

**MYRRH.** This gum-resin exudes from the bark of the *Balsamodendron myrrha*; it appears to have been an object of trade with the Eastern nations more than 3500 years ago (Genesis, xxxvii. 25), but nothing was known of the tree which yields it till the return of Ehrenberg from his travels in Africa and Asia, in 1825, who brought a specimen of it from Gison, on the borders of Arabia Felix, which has been figured and described by Nees von Esenbeck, under the above name. (PEREIRA, *Mat. Med.*) The gum-resin is imported from the East Indies in large agglomerated tears, of a reddish-brown, or brownish-yellow color, semitransparent, and having a dull and somewhat fatty kind of fracture; they are often veined, striated, and mottled; of a peculiar balsamic and fragrant odor, and of a bitter, aromatic, and somewhat pungent taste. Fragments of other gums and resins are frequently found in the chests of myrrh. It consists, according to Pelletier, (*Ann. de Chim.*, LXXX. 45), usually of from 30 to 40 *per cent.* of resin, and from 60 to 70 *per cent.* of gum; it also contains a volatile oil, obtained, to the amount of from 2



to 3 per cent., by distilling myrrh with water. According to Ruickholdt (*Archiv. für Pharmazie*, xci. 1), the best myrrh contains between 44 and 45 per cent. of resin, which is of a brown color, fusible below  $212^{\circ}$ , and retains a slight odor and taste of myrrh. By heating it, Ruickholdt obtained a modified resin, which he terms *myrrhic acid*.

**OLIBANUM.** This gum-resin is the produce of the *Boswellia thuiifera*, growing in the mountainous parts of Coromandel; it was termed *frankincense* by the ancients, and used in their religious ceremonies: it is noticed by Moses. (Exodus xxx. 34.) Dioscorides calls it *λίβανος*. Olibanum is imported from India in "round, oblong, or ovate, pale yellowish, semiopaque, fragile tears, having a balsamic resinous odor." (PEREIRA.) According to Johnston (*Phil. Trans.*, 1839, p. 301), when the olibanum of the shops, the lumps of which differ apparently only in depth of color, is introduced into alcohol, some pieces are rendered transparent, while others become white and opaque, from a powdery coating left upon their surface. The latter contain an acid resin =  $C_{40}H_{32}O_6$ , constituting the larger portion of the olibanum of commerce, and associated with a variable quantity of volatile oil. The clearer and yellower pieces give less gum than the others, and contain a resin represented by  $C_{40}H_{32}O_4$ , and having considerable resemblance, in smell and other properties, to colophony.

**OLIVE TREE GUM.** This term has been applied to a substance which exudes from the bark of the wild olive trees of the South of Italy, and Sardinia. In Calabria it is called *Lecca gum*, from a town in that country, near which it is abundantly produced. Pelletier, who first examined this product, in 1816, (*Ann. Ch. et Ph.*, iii. 105, and li. 196), discovered in it a principle which he has termed *olivile*, and which is obtained by digesting the pulverized olive-gum in ether for 24 hours, and then boiling the residue in alcohol, and filtering whilst hot; on cooling, the liquor concretes into a crystalline mass of olivile, which must be drained on a filter, and washed with cold alcohol.

*Olivile* is white, inodorous, and of a sweetish-bitter taste; when crystallized from its alcoholic solution, it forms stellated groups of prisms which include, according to Sobrero (*Ann. der Pharm.*, liv. 67), 2 atoms of water, 1 of which is abstracted by dessication *in vacuo*. When this monohydrate is fused, anhydrous olivile remains. Crystallized olivile is little soluble in cold water, and requires for its solution 32 parts of boiling water; it is very soluble in boiling alcohol, from which, when pure, it separates on cooling, in crystals: but if impure, from the presence of resin, it is deposited in the form of a white granular powder. According to Sobrero, it dissolves in ether, and in fat and volatile oils. When olivile is heated to  $160^{\circ}$ , with less water than is required for its solution, the undissolved portion fuses, and covers the bottom of the vessel, in the form of a heavy oil, which concretes into a crystalline mass on cooling. The pure crystallized olivile fuses at about  $245^{\circ}$ , and concretes into an amorphous resin-like substance, which is highly idioelectrical, and which is now fusible at  $158^{\circ}$ . When olivile is heated upon platinum foil, white acid fumes of a benzoic odor are evolved, and it burns with a smoky flame. By dry distillation, water, and an oily acid are obtained:

this acid Sobrero terms *pyrolivilic acid*, and assigns to it the formula  $C_{20}H_{13}O_5$ . The formula of *anhydrous olivile*, deduced from its latest analysis by Sobrero, is  $C_{28}H_{18}O_{10}$ ; Pelletier's results do not, however, quite agree with this estimate.

|                        |    |      |     |      |        | Sobrero.   | Pelletier. |
|------------------------|----|------|-----|------|--------|------------|------------|
| Carbon .....           | 28 | .... | 168 | .... | 63.16  | .... 63.17 | .... 63.84 |
| Hydrogen .....         | 18 | .... | 18  | .... | 6.76   | .... 6.80  | .... 8.06  |
| Oxygen .....           | 10 | .... | 80  | .... | 30.08  | .... 30.03 | .... 28.10 |
| <hr/>                  |    |      |     |      |        |            |            |
| Anhydrous olivile .... | 1  |      | 266 |      | 100.00 | 100.00     | 100.00     |

By adding ammonia to a mixed solution of olivile and nitrate of lead, Sobrero obtained a precipitate, which, when washed, and dried at  $268^{\circ}$ , consisted of  $2PbO$ ,  $C_{28}H_{18}O_{10}$ .

OPOPONAX is the gum-resinous exudation of *Opoponax chironium*, a plant resembling the parsnip, growing in the sunny parts of the south of France, Italy, Sicily, Croatia, and Greece. Opoponax occurs in reddish tears or pieces, of a peculiar fusty and unpleasant odor, and an acrid and bitter taste. It contains, according to Pelletier, about 42 *per cent.* of resin, and 33 of gum, the remainder being extractive matter, starch, lignine, and from 5 to 6 *per cent.* of volatile oil. The alcoholic tincture of opoponax leaves, when evaporated, a dark-brown resin, of a peculiar odor, fusible at  $212^{\circ}$ , and which is easily decomposed by heat. Johnston assigns the formula  $C_{40}H_{25}O_{14}$  to this resin, as it exists in the natural gum-resin of commerce.

SAGAPENUM. Nothing is known respecting the plant which yields this gum-resin. The finest kind consists of masses made up of agglutinated brownish-yellow semitransparent tears, and resembling galbanum, but having a darker color, and a more alliaceous odor. It has a hot acrid taste, and when heated exhales a more aromatic and agreeable odor than galbanum. It is imported from the Levant. (PEREIRA.) According to Brandes, it contains about 50 *per cent.* of resin, and 33 of gum; when distilled with water, it yields from 3 to 4 *per cent.* of volatile oil. The resin of sagapenum is pale yellow, of a strong garlic odor, fuses readily, and becomes fluid at  $212^{\circ}$ ; it may be represented by  $C_{40}H_{29}O_9$ . (JOHNSTON.)

ALOE. This substance is the produce of several species of *aloe*, especially *Aloe vulgaris*, *Socotrina*, and *spicata*; the plant is a native of the East Indies and Barbary, and is cultivated in the West Indies, and in Italy, Sicily, and Malta. The finest aloes is obtained by evaporating the juice which flows spontaneously from the transversely cut leaves; and afterwards, the leaves are boiled, and yield a common variety, in the form of extract. The different kinds of aloes differ in appearance. *Socotrine aloes* is in reddish-brown masses, translucent, and of a smooth conchoidal fracture; its taste is very bitter, and its odor fragrant and aromatic; its powder is deep brownish-yellow; when heated, it also exhales an agreeable odor. *Barbadoes aloes* is imported in large gourds, and in masses; it is reddish-brown, or very dark brown, and its fracture generally rather dull than glossy. It has a peculiarly unpleasant odor, which is much increased by breathing on it; its powder is of a



dull olive-yellow or brown color. Its taste is nauseously bitter. Aloes is soluble both in alcohol and in boiling water; its hot saturated aqueous solution deposits a pulverulent brown substance on cooling, which is again soluble in boiling water.

*Bitter principle of Aloes. Aloetine.* This substance constitutes about 60 per cent. of ordinary aloes, and is soluble in cold water; it is regarded as the purgative principle of aloes; the insoluble residue is the same as the brown matter which a decoction of aloes deposits on cooling; it is sometimes termed a *resinoid*, and the stimulating and griping effect of aloes has been ascribed to it.

When the cold aqueous infusion of aloes is evaporated, it leaves a brown transparent residue, or extract, very bitter, readily soluble in water and in alcohol, but less soluble in ether. Its aqueous solution, which has no acid reaction, yields a resinous deposit when mixed with sulphuric acid. This aqueous infusion of aloes (prepared without heat) gives a brown precipitate with acetate of lead, and when this is separated by filtration, basic acetate of lead occasions a fresh precipitate in the filtrated liquor. The alkalis, and the persalts of iron, darken the tint of this infusion.

*Resin of aloes* is the term generally applied to that portion of aloes which is insoluble in cold water, or which falls on cooling its decoction; but its solubility in boiling water shows that it is not a resin; it appears to be formed by the action of air upon the preceding extractive; it dissolves in the alkalis, and in lime water, and is thrown down again from these solutions by the acids.

When aloes is subjected to dry distillation, or when it is heated with caustic potassa, it affords abundance of ammonia, so that it contains nitrogen, but neither its proximate nor its ultimate composition have as yet been satisfactorily studied.

*Products of the decomposition of Aloes by Nitric Acid.* These vary with the strength of the acid, its temperature, and the duration of its action. When the acid is dilute, it yields *artificial aloe-bitter*; and this, by the continued action of a stronger acid, passes into *chrysammic acid*, and afterwards into *chrysolepic acid*. Braconnot (*Journ. de Physique*, lxxxiv. 334, 1817), Schunck (*Revue Scientifique*, vii. 231), and Liebig (*Traite de Chim. Org.*, ii. 540), are the principal chemists who have examined these products.

1. *Artificial aloe-bitter. Polychromatic acid.* One part of aloes is heated in a retort with 8 parts of nitric acid, of sp. gr. 1.25; violent action ensues, attended by the disengagement of nitrous vapor, and a yellow solution is obtained, which, on dilution with cold water, deposits impure *aloe-bitter*; it is purified by repeated washing with water, which should be continued till the washings acquire a purple color; they carry off a considerable portion of oxalic acid. When dulyedulcorated, aloe-bitter is a brown powder, bitter, and very astringent, and reddens litmus. It dissolves in from 800 to 850 parts of cold water, forming a purple solution; hot water takes it up more abundantly. Its solution is rendered yellow by the acids. By dry distillation it is decomposed with explosion and evolution of light. It dissolves, with the aid of heat, in the dilute acids, but separates on cooling, or on the addition of water. Its hot aqueous solution communicates a dark brownish-purple tint to



silk, which, if previously mordanted with the salts of copper, of tin, or with alum, is dyed of all shades of brown, blue, violet, green, and yellow, which bear washing, but gradually fade under the influence of light. The dye upon wool is of a dingy red.

When a solution of chloride of barium is added to a solution of aloebitter in an alkali, a reddish-brown precipitate falls, and the supernatant liquor acquires a deep red color. The precipitate and the liquor contain two distinct substances, having acid characters, and which appear to be constituent or proximate principles of the aloebitter; the one has been termed by Schunck, *aloetinic* (or *aloetic*), and the other *aloeretic* acid.

The *aloeretic* acid is in combination with the baryta, and may be extracted by means of nitric acid; its combinations with the oxides of the heavy metals are mostly brown and insoluble; those with potassa and soda are not crystallizable, and when evaporated, leave thick, gelatinous, brown masses.

*Aloetinic* acid (*aloetic*) is obtained by adding nitric acid to the filtrate from the barytic precipitate; it is then deposited in the form of a yellow powder, which produces red, and mostly soluble salts, with the bases. The saturated potassic solution of this acid affords, on evaporation and cooling, brilliant needles of a deep blood-red color; if spontaneously evaporated, the crystals are more perfect, and of a ruby color. The composition of these acids has not been determined.

*Chrysammic* acid (*χρυσος*, *gold*, and *αμμος*, *sand*),  $C_{15}H O_{12} N_2 + HO$ . This acid is prepared by heating a mixture of 1 part of aloes and 8 parts of nitric acid, sp. gr. 1·37, in a porcelain basin, till the violent reaction is over; the liquor is then poured into a retort, and two-thirds of the nitric acid are distilled off; 3 or 4 parts more of nitric acid are then added to the residue, and the whole left for some days at a temperature approaching its boiling-point, or as long as any gas continues to be evolved. When the greater part of the nitric acid has thus been volatilized, water is added to the residue as long as it occasions a precipitate. The precipitate is chrysammic acid; the supernatant liquor holds chrysolepic and oxalic acid in solution.

The chrysammic acid thus obtained is impure; it includes nitric, and chrysolepic acid, and if a sufficiency of nitric acid has not been employed, it also contains aloetinic and aloeretic acids. The first of these are removed by abundant ablutions, when the chrysammic acid remains in the form of a brilliant powder, granular, and greenish-yellow; when contaminated by aloetinic and aloeretic acid, it never presents this appearance. The formula assigned to this acid by Löwig is  $HO + C_{15}H O_4, 2NO_4$ . Its ultimate elements are

|  |        | Schunck. Pelouze. |       |        |        |       |      |       |                                       |       |         |       |
|--|--------|-------------------|-------|--------|--------|-------|------|-------|---------------------------------------|-------|---------|-------|
| Carbon.....                              | 15.... | 90....            | 40·18 | ....   | 40·39  | ....  | 40·0 | } = { | Anhydrous<br>chrysammic<br>acid ..... | 1.... | 215.... | 95·9  |
| Hydrogen ...                             | 2....  | 2....             | 0·89  | ....   | 1·15   | ....  | 1·1  |       |                                       |       |         |       |
| Oxygen .....                             | 13.... | 104....           | 46·43 | ....   | 45·99  | ....  | 46·7 |       |                                       |       |         |       |
| Nitrogen .....                           | 2....  | 28....            | 12·50 | ....   | 12·47  | ....  | 12·2 |       |                                       |       |         |       |
| <hr/>                                    |        |                   |       |        |        |       |      |       |                                       |       |         |       |
| Crystallized<br>chrysammic<br>acid ..... | } 1    |                   | 224   | 100·00 | 100·00 | 100·0 |      |       |                                       | 1     | 224     | 100·0 |

Chrysammic acid is very sparingly soluble in water; it forms a red



and bitter liquor; it is soluble in alcohol and in ether, and in the hot mineral acids. When adequately heated, it explodes with violence, producing flame, and evolving the odor of bitter almonds, together with nitrous vapor; when heated in chlorine it produces hydrochloric acid. Fused with potassa, or boiled in a strong solution of caustic potassa, it evolves ammonia. When its solution in nitric acid is heated, much gas is evolved, and after protracted ebullition, small golden-yellow scales are deposited on cooling, which produce a compound with potassa which is insoluble in water, and with soda a soluble compound which crystallizes in golden-green needles. Heated with sulphuric acid it evolves no sulphurous acid, but forms a brown solution, which, after dilution with water, deposits, on cooling, very brilliant grey acicular crystals, which form a brown solution with water. When their solution is mixed with nitric acid, brilliant yellow scales are formed, which differ from chrysammic acid. In the salts of chrysammic acid with potassa, soda, and oxide of lead, the atom of water of the hydrated acid is replaced by an atom of the metallic oxide. The *chrysammates* are characterized by their sparing solubility, and by exploding when heated; they are decomposed by the mineral acids, and chrysammic acid is set free. When rubbed with a burnisher they assume a yellow metallic lustre.

*Chrysammate of Ammonia.* When chrysammic acid is digested in a hot aqueous solution of ammonia, it forms a dark purple liquor, which, on cooling, deposits small dark-green acicular crystals. If nitric acid be added to the hot solution, it becomes purple-red, and no chrysammic acid is thrown down, but, on cooling, small black brilliant scales are formed, which pass into chrysammic acid when long boiled in nitric acid. When the ammonia compound is added to the salts of baryta, copper, lead, or silver, the resulting products are quite different from the true chrysammates: but when it is boiled with potassa, ammonia is evolved, and chrysammate of potassa formed. The actual composition of this so-called chrysammate of ammonia has not been determined.

*Chrysammate of Potassa* separates from its boiling solution in small golden-green crystalline plates; if the liquor be very quickly cooled, the salt falls in the form of a carmine-red powder, composed of brilliant microscopic crystals. It is tolerably soluble in boiling water, but requires 1250 parts of water at  $60^{\circ}$  for its solution, which is of a fine red color. According to Schunck, the components of this salt are  $\text{KO}, \text{C}_{15} \text{H O}_{12} \text{N}_2$ ; or  $\text{KO} + \text{C}_{15} \text{H O}_4, 2 \text{NO}_4$ ; its equivalent is 233.

*Chrysammate of Soda* and *Chrysammate of Magnesia* resemble the potassa-salt.

*Chrysammate of Lime* and *Chrysammate of Baryta* are bright-red granular precipitates, almost insoluble in water.

*Chrysammate of Zinc* and *Chrysammate of Copper* are soluble in boiling water, and fall, on cooling, in the form of slender needles.

*Chrysammate of Lead*,  $\text{PbO}, + \text{C}_{15} \text{H O}_4, 2 \text{NO}_4$ , is an insoluble red powder; so also is *Chrysammate of Silver*.

*Chrysolepic acid* is obtained by evaporating the mother-liquor and the washings obtained in the preparation of chrysammic acid; the crystals which are deposited are washed to separate oxalic acid, and the residue is *chrysolepic acid*; when pure, it forms delicate yellow crystalline scales, but it is sometimes mixed with aloë-bitter, which is a yellow uncrys-

talline powder. The crystals of chrysolepic acid are of a golden yellow color, little soluble in cold, but more abundantly in boiling water, and from this solution the acid falls on cooling in the state of a dull-yellow powder; it may be dissolved in, and crystallized from nitric acid, without change. When rapidly heated it is decomposed with explosion. This acid has many properties in common with nitropicric acid, with which, according to Schunck, it is isomeric, if not identical; its formula is  $\text{HO}, + \text{C}_{12}\text{H}_2\text{O}, 3\text{NO}_4$ : but when a boiling concentrated solution of chrysolepate of soda is mixed with acetate of lead, brilliant yellow scales are deposited, composed of basic chrysolepate combined with neutral acetate of lead. When these crystals are boiled with water they lose their crystalline aspect, and are transformed into a yellow powder, which redissolves in excess of a saturated solution of acetate of lead, and again yields the same crystals. These crystals are easily soluble in dilute acetic acid, and when this solution is evaporated to the consistence of syrup, it deposits small brown scales, of a metallic lustre, which are probably a neutral chrysolepate of lead. The formation of these salts of lead is, according to Liebig, characteristic of chrysolepic acid; for when nitropicrate of potassa is added to acetate of lead, a yellow pulverulent precipitate falls, which is scarcely soluble in water.

According to E. Robiquet, (*Ann. Ch. et Ph.*, 3ème Sér., xx. 483,) the substance which forms the bulk of the finest aloes, and which has been above termed *Aloetine*, should be regarded as a *coloring-matter*, combined with a small portion of ulmate of potassa, phosphate, sulphate, and carbonate of lime, gallic acid, and vegetable albumine. Aloetine consists of 27.39 per cent. of carbon, 11.11 of hydrogen, and 61.50 of oxygen, and, when free from albumine, contains no nitrogen. He further observes, that chrysammic acid, when dissolved in ammonia, and heated to  $212^\circ$ , gives rise to the production of an amide-acid, which he terms *Chrysammamic acid*, and which, when boiled with dilute sulphuric, or nitric acid, is converted into *chrysammalide*. By the dry distillation of aloes with lime, E. Robiquet obtained an oily liquid (*aloisole*), together with abundant evolution of inflammable gases. Aloisole is a pale-yellow liquid, very greedy of oxygen; its odor partakes of that of potato-oil, and bitter-almond oil: its chemical actions are those of an aldehyde. By the action of oxidizing agents, it is transformed either into bitter-almond oil, water, and carbonic acid; or into *aloisic acid*, which is a brown oily liquid, having the odor of castor. By the action of a current of chlorine upon an aqueous or an alcoholic solution of aloes, two compounds are obtained, one of which, *chloraloile*, contains no hydrogen; the other contains hydrogen, and is easily decomposed by heat.

*Nitrostyphnic Acid.* By the action of nitric acid upon certain gum resins, Böttger and Will (*Ann. der Pharm.*) obtained a compound which they have termed *styphnic acid* (from  $\sigma\tau\upsilon\phi\nu\sigma$ , *astringent*). It has been designated *nitrostyphnic acid* by Berzelius, and appears to be identical with the acid described by Erdmann (*Erdmann and Marchand's Journ.*, xxxvii. 409), obtained by the action of nitric acid upon euxanthine and euxanthone (p. 1526). Löwig describes this acid under the name of *oxynitropicric acid*, in reference to its composition, which may be represented as  $\text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4$ ; nitropicric acid (p. 1488), being  $\text{C}_{12}\text{H}_2\text{O}, 3\text{NO}_4$ . It may



also be obtained from most of the resins and volatile oils, and from several extracts; but not from styrax, dragon's blood, or opoponax. It is procured in the greatest abundance from ammoniacum and from asafoetida, especially from the latter. The following directions are given by Böttger and Will for its preparation: Pieces of asafoetida of the size of walnuts are put into a large porcelain basin, together with 5 or 6 parts of diluted nitric acid, of sp. gr. 1.2; the mixture is then heated to  $160^{\circ}$  or  $165^{\circ}$ , and removed from the fire, when a violent action soon commences, and a yellow scum collects upon the surface of the liquor, which increases so as to require constant stirring to keep it down, and at length subsides into a lemon-yellow mass as tough as bird-lime. The basin is then returned to the sand-heat, and boiled till the whole of the product is dissolved, fresh portions of the acid being occasionally added to compensate for loss by evaporation. The operation is generally complete in 5 or 6 hours, or in half the time, if stronger nitric acid be added. When the product is of the consistence of thin syrup, and of a reddish-brown color, a little of it is tested by diluting it with water, and if a yellow sandy powder falls, the boiling has been continued long enough; but if the precipitate is flocculent, the boiling must be resumed, till, on testing, it is found to have acquired its proper character. The nitric acid is then, as far as may be, driven off in a water-bath, the residue well mixed with a large quantity of boiling water, and carbonate of potassa added so as just to neutralize the acid. Excess of the alkali must be avoided, as it would dissolve a portion of the resinous matter which the neutralization has separated, and which floats upon the surface: if this were redissolved by the alkali, the liquor would be rendered dark-brown. The liquor is then filtered through coarse paper, somewhat evaporated, and set aside to crystallize, when a brown pellicle of nitrostyphnate of potassa is formed, and more of which is obtained by further evaporation, till at last a dark-brown mother-liquor remains which only yields crystals of nitre. The brown salt is dissolved in boiling water, decolorized by animal charcoal, and recrystallized: when thus purified, it is again dissolved, and decomposed by slight excess of nitric acid, which throws down the nitrostyphnic acid, at first pulverulent, and afterwards crystalline; after having been washed with a little cold water, it is to be dried, and dissolved in boiling absolute alcohol, which, on cooling, deposits it in the course of a few hours in pale yellow prismatic crystals.

This acid has an astringent taste, and, when heated, loses water, fuses, and concretes on cooling into a crystalline mass; at a higher temperature it partly sublimes and is partly decomposed; it burns in the air with a brilliant flame, and leaves a carbonaceous residue; when suddenly and strongly heated, it deflagrates like gunpowder. It requires about 100 of water at  $75^{\circ}$  for solution, and about 88 parts at  $145^{\circ}$ . It is readily soluble in alcohol and in ether. It is soluble without change in hot nitric acid. It is not very soluble in boiling hydrochloric acid, nor does it evolve chlorine when so dissolved. It is not more soluble in acetic acid than in water. Its solutions tinge the cuticle yellow. Boiled in nitrohydrochloric acid, it is decomposed, and yields oxalic acid. Boiling sulphuric acid also decomposes it. (BÖTTGER and WILL.) By the joint action of hydrochloric acid and chlorate of potassa, it produces chloranile. (HOFMANN.)

*Crystallized Nitrostyphnic Acid*, dried at  $212^{\circ}$ , consists of

|   |        | Böttger and |       | Will.  |        | Erdmann. |       |       |                        |       |         |        |
|---|--------|-------------|-------|--------|--------|----------|-------|-------|------------------------|-------|---------|--------|
| Carbon .....                                | 12.... | 72....      | 29.38 | ....   | 29.33  | ....     | 29.58 | } = { | Anhydrous<br>acid..... | 1.... | 236.... | 96.33  |
| Hydrogen .....                              | 3....  | 3 ..        | 1.22  | ....   | 1.39   | ....     | 1.26  |       |                        |       |         |        |
| Oxygen .....                                | 16.... | 128....     | 52.25 | ....   | 52.41  | ....     | 51.86 |       | Water ...              | 1.... | 9....   | 3.67   |
| Nitrogen .....                              | 3....  | 42....      | 17.15 | ....   | 16.87  | ....     | 17.30 |       |                        |       |         |        |
| <hr/>                                       |        |             |       |        |        |          |       |       |                        |       |         |        |
| Crystallized<br>nitrostyphnic<br>acid ..... | }      | 1           | 245   | 100.00 | 100.00 | 100.00   |       |       |                        | 1     | 245     | 100.00 |
|   |        |             |       |        |        |          |       |       |                        |       |         |        |

*Salts of the Nitrostyphnic Acid.* This acid, when aided by heat, expels carbonic acid from the carbonates, so that its salts are easily obtained by saturating a hot solution of the acid by a carbonate of the base. The *neutral* nitrostyphnates contain 2 atoms of basis, one of which may be replaced by an atom of a different base, so therefore as to give rise to a very numerous class of double salts. These salts are mostly yellow or orange-colored, have a bitter taste, and are violently explosive when rapidly heated. The neutral salts of most of the bases are more or less soluble in water. The salts of the alkalis are mostly thrown down from their solutions in water by the addition of excess of the alkali, whether caustic or carbonated, and, generally speaking they are more soluble than the corresponding *nitropicrates*. Many of the neutral (bibasic) nitrostyphnates combine with an additional equivalent of acid to form *acid* (or monobasic) salts; they are somewhat less soluble in water than the corresponding neutral (or bibasic) salts, and of a paler yellow color; when heated, a part of their acid first sublimes, and the residue then explodes. The above-mentioned *double salts* are formed by saturating a boiling aqueous solution of the monobasic, or acid salts, with another basic carbonate, as for instance of copper, nickel, or cobalt; and they have this peculiarity, that when their solutions are digested with animal charcoal, the weaker base is separated, and the acid salt of the stronger base remains dissolved. A general analogy pervades the nitrostyphnates and nitropicrates, so that they are not easily distinguished; but when treated with sulphate of iron and hydrate of baryta, the nitropicrates are *reddened*, but the nitrostyphnates acquire a *dark-green* color.

*Nitrostyphnate of Ammonia.* The *neutral* (or bibasic) salt is tolerably soluble in pure water, and crystallizes in large orange-colored needles, which are anhydrous. The components of this salt are represented, according to the analyses of Böttger and Will, and of Erdmann, by  $C_{12}H_9O_{16}N_5$ , or by the formula  $NH_4O, NH_3, + C_{12}H_2O_3, 3NO_4$ . The *acid* (or monobasic) salt may be obtained by crystallization from its weak solution, in long flat pale-yellow needles; but when its concentrated solution is rapidly cooled, it forms minute interwoven capillary crystals, composed of  $NH_4O; + C_{12}H_2O_3, 3NO_4; + 2HO$ . Both these salts deflagrate when heated.

*Nitrostyphnate of Potassa.* (*Bibasic.*) This salt is obtained by saturating a warm solution of the acid, with carbonate of potassa; on cooling, it forms radiated tufts of acicular crystals, of a pale-yellow color, very sparingly soluble in water, and insoluble in a solution of caustic or carbonated potassa. The formula assigned by Löwig (upon the authority



of Böttger and Will) to this salt, is  $2\text{KO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4$ . The *monobasic* salt forms small interwoven acicular crystals, which dry into a sandy powder. From a weak solution it may be obtained in well-defined prisms. When heated, a portion of its acid sublimes, and it then explodes with violence. Its formula is  $\text{KO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4; + 2\text{HO}$ . Dried at  $212^\circ$  it loses its water of crystallization.

*Nitrostyphnate of Soda* crystallizes in small pale-yellow needles, which often aggregate into globular groups; it is very soluble, and contains 13.3 *per cent.* of water of crystallization, which it loses at  $212^\circ$ . Its formula is  $2\text{NaO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4 + 5\text{HO}$ .

*Nitrostyphnate of Lime* is easily soluble, and forms aggregates of pale yellow needles, containing 7 atoms of water, 4 of which are driven off at  $212^\circ$ .

*Nitrostyphnate of Baryta*,  $2\text{BaO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4 + 4\text{HO}$ , crystallizes in delicate orange-colored prisms, difficultly soluble in water, and powerfully explosive when heated. This salt contains 4 atoms of water, 2 of which are expelled at  $212^\circ$ .

*Nitrostyphnate of Strontia*,  $2\text{SrO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4, + 4\text{HO}$ , crystallizes in bulky spherical aggregates of thin long pale-yellow acicular prisms, more soluble in water than the baryta salt, and retaining 1 atom of water, after desiccation at  $212^\circ$ .

*Nitrostyphnate of Magnesia* is a very soluble and difficultly crystallizable salt.

*Nitrostyphnate of Manganese*,  $\text{MnO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4, + 12\text{HO}$ , is best obtained by double decomposition, from nitrostyphnate of baryta and sulphate of protoxide of manganese: when its concentrated solution is evaporated over sulphuric acid, it often forms large thick rhombic tables, of a pale-yellow color, and easily soluble. Dried at  $212^\circ$ , these crystals lose 10 atoms of water, and retain 2.

*Nitrostyphnate of Protoxide of Iron* is a very soluble, difficultly crystallizable salt; it easily oxidizes by exposure to air.

*Nitrostyphnate of Zinc* is an extremely soluble deliquescent salt: the formula assigned to it by Böttger and Will is  $5\text{ZnO}, + 2[\text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4,] + 8\text{HO}$ .

*Nitrostyphnate of Cadmium* is very deliquescent; both it and the zinc salt are only slightly explosive when heated.

*Nitrostyphnate of Cobalt*,  $2\text{CoO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4, + 7\text{HO}$ , is very soluble, and crystallizes in groups of brown acicular crystals. It is extremely explosive. Dried at  $212^\circ$ , it loses 3, and retains 4 atoms of water. When the monobasic potassa salt is saturated with carbonate of cobalt, a bibasic salt is obtained,  $= \text{KO}, \text{CoO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4, + 4\text{HO}$ . Analogous salts are produced with oxide of *nickel*.

*Nitrostyphnate of Copper*,  $2\text{CuO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4, + 8\text{HO}$ , crystallizes in pale-green needles; they lose 6 atoms of water when dried at  $212^\circ$ , and are powerfully explosive when heated. There is an *ammonio-nitrostyphnate of copper*  $= \text{NH}_4\text{O}, \text{CuO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4, + 7\text{HO}$ ; and a *potassio-nitrostyphnate of copper*,  $= \text{KO}, \text{CuO}, + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4, + 4\text{HO}$ .

*Nitrostyphnate of Lead* has only been obtained in the form of a basic salt, which is obtained by dropping a solution of the acid into a solution of acetate of lead; it is a pale-yellow flocculent precipitate, very explo-

sive, not only by heat, but also by friction; after having been dried at  $212^{\circ}$ , it retains 2 atoms of water, and is represented, according to the analysis of Böttger and Will, by  $4\text{PbO} + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4 + 2\text{HO}$ .

*Nitrostyphnate of Silver.* When a moderately concentrated solution of nitrate of silver is heated up to  $140^{\circ}$ , and mixed with a solution of the bibasic potassa salt, difficultly soluble and bulky crystals, of a pale-yellow color, are soon formed; they are aggregates of acicular prisms. When their solution is boiled, they are decomposed, and metallic silver is deposited. Their formula is  $2\text{AgO} + \text{C}_{12}\text{H}_2\text{O}_3, 3\text{NO}_4 + \text{HO}$ .

## BALSAMS.

**COPAIVA BALSAM.** This product is obtained from various species of *Copaifera*, trees growing principally in the Brazils, and in the province of Para, from whence, and from Maranhão, the balsam is chiefly procured. It flows abundantly from incisions in the stems. It is a clear transparent liquid of about the consistence of olive-oil, but thickens with age. It has a pale-yellow color; a peculiar and somewhat fragrant odor, and a bitterish, warm, and nauseous taste; its sp. gr. is generally between 0.95 and 0.97. It is insoluble in water, but soluble in alcohol, in ether, and in fixed and volatile oils. It contains from 30 to 40 per cent. of essential oil, the remainder being principally resinous.

*The essential oil of Copaiva* is obtained by distilling the balsam, either alone, or with water. When rectified over chloride of calcium, it is a thin colorless oil, of an aromatic odor; its sp. gr. is 0.885, and its boiling-point between  $470^{\circ}$  and  $500^{\circ}$ . It mixes in all proportions with alcohol and with ether. It belongs to the class of hydrocarbons  $=\text{C}_{10}\text{H}_8$ ; it combines with hydrochloric acid, forming *Copaiva-camphor*  $=\text{C}_{10}\text{H}_9\text{Cl}$ . (SOUBEIRAN and CAPITAINÉ, *Ann. der Pharm.*, xxxiv. 321. BLANCHET, *Ibid.*, vii. 158.)

*Resin of Copaiva* remains after the separation of the volatile oil by distillation. It is separable, by the action of naphtha, into a soluble acid resin (*copaivic acid*), and an insoluble indifferent resin.

*Copaivic Acid*,  $\text{C}_{40}\text{H}_{30}\text{O}_4$ , is obtained by shaking together 9 parts of copaiva balsam with 2 parts of solution of caustic ammonia, of sp. gr. 0.95, and leaving the mixture for a long time at a temperature of  $50^{\circ}$ . The crystals which form are to be washed with ether, and then dissolved in alcohol and left to spontaneous evaporation. (SCHWEITZER, *Poggend. Ann.*, xvii. 487.) This acid resin may also be obtained by digesting the resin of copaiva, as above mentioned, in naphtha, evaporating the solution, dissolving the residuary copaivic acid in alcohol, and crystallizing. This acid forms small soft prismatic crystals, soluble in alcohol, ether, and in fat and volatile oils, and in sulphuret of carbon. The alcoholic solution reddens litmus. Copaivic acid has been analyzed by Rose, (*Poggend. Journ.*, xxxiii. 37; and liii. 372,) and by Hess, (*Ibid.*, xlvii. 319,) with the following results:

|                    |    |      |     |      |        | Rose.  | Hess.  |
|--------------------|----|------|-----|------|--------|--------|--------|
| Carbon .....       | 40 | .... | 240 | .... | 79.47  | ....   | 79.12  |
| Hydrogen .....     | 30 | .... | 30  | .... | 9.93   | ....   | 10.01  |
| Oxygen .....       | 4  | .... | 32  | .... | 10.60  | ....   | 10.87  |
| <hr/>              |    |      |     |      |        |        |        |
| Copaivic acid..... | 1  |      | 302 |      | 100.00 | 100.00 | 100.00 |



*Salts of the Copaivic Acid.* An alcoholic solution of this acid is not precipitated by potassa, or soda. When it is added to an alcoholic solution of acetate of lead, a crystalline precipitate falls,  $=\text{PbO}, + \text{C}_{40}\text{H}_{30}\text{O}_4$ . The alcoholic solution of the acid, added to an alcoholic solution of nitrate of silver, occasions no precipitate till ammonia is added, when a white crystalline powder falls, which blackens in the light, fuses like a resin, and is difficultly soluble in alcohol, but readily in ammonia.

Fehling has examined a crystalline deposit which he found in copaiva balsam, from Para (*Para balsam*.) By the spontaneous evaporation of its alcoholic solution, he obtained it in regular crystals, becoming electric by friction, fusible at  $250^\circ$ , and readily soluble in ether. The composition of this crystalline resin is  $\text{C}_{40}\text{H}_{28}\text{O}_6$ . He also obtained it in the state of a hydrate,  $=\text{C}_{40}\text{H}_{30}\text{O}_8$ . (*Ann. der Pharm.*, XL. 110.)

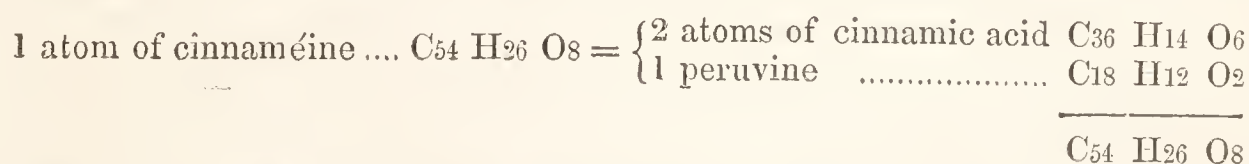
*Mecca Balsam* is the produce of the *Amyris Gileadensis*, (*Balsamodendron Gileadense*,) growing at Gilead in Judea. It is also called *opobalsamum*. It has been examined by Vauquelin (*Annales de Chimie*, XLIX. 231,) by Trommsdorff (THOMSON'S *Veg. Chem.*, p. 523,) and by Bonastre (*Journ. de Pharm.*, xviii. 95.) Its sp. gr. is about 0.950; it has a peculiar fragrant odor, and rapidly thickens on exposure to air, assuming the color and consistence of turpentine. When distilled with water it yields about 30 per cent. of an agreeably smelling volatile oil, of an acrid taste, which, by the action of nitric acid, is converted into a resin having the odor of musk. The remaining resin is separable by alcohol into a *hard resin*, which dissolves, and which leaves about 4 per cent. of a *soft resin*, insoluble in cold alcohol, but soluble in oils. From a sample of genuine *opobalsamum*, Bonastre only obtained 10 per cent. of volatile oil; but as this product is resinified by exposure to air, its proportion, in different specimens, will be liable to much variation. Bonastre has termed the insoluble resin *Burserine*, from its resemblance to the insoluble portion of the balsam of *Bursera gummifera*.

PERU BALSAM is said to be the produce of the *Myrospermum Peruiferum*, a branching elegant tree, growing in Peru, New Granada, Columbia, and Mexico; but how the balsam is obtained, whether by incision, or by boiling the bark and branches in water, or by the aid of a higher temperature, is by no means evident. It is imported in canisters, and in earthen pots, from Valparaiso and other places. It is a transparent deep-brown or blackish liquid, of the consistence of treacle; it has an agreeable balsamic odor, especially when heated, and a pungent and somewhat bitter taste. Its sp. gr. varies from 1.150 to 1.160. There is an article known under the name of *white balsam of Peru*, which is probably identical with the balsam termed *liquidambar*, procured in Mexico and Louisiana from the stem of *Liquidambar styraciflua*.

Balsam of Peru has been examined by several chemists: the most recent analysis of the *black balsam* is by Fremy. (*Ann. Ch. et Ph.*, LXX. 182.) Some of his results, as well as those of Plantamour, have been already quoted under the head of *Cinnamic acid*, (p. 1390.) The components of Peruvian balsam are, according to Fremy, 1. an oily matter, which he terms *cinnaméine*, and which frequently contains a crystallizable

substance, (*metacinnaméine*.) 2. *Cinnamic acid*. 3. One or more *resins*.

When Peruvian balsam is dissolved in alcohol, and the solution mixed with an alcoholic solution of potassa, cinnamate of potassa and cinnaméine are retained in solution, and the compound of the resin with potassa remains undissolved. On adding water to the alcoholic solution, the cinnaméine separates and floats upon the surface; the formula assigned to it being, as already stated,  $C_{54}H_{26}O_8$ . It is a brown, inodorous, acrid oil, soluble in alcohol and ether, and insoluble in water. Sulphuric acid converts it into a resin, fusible at  $212^{\circ}$ . It is as it were saponified, by a weak solution of caustic potassa, and converted into cinnamic acid, and a light oily fluid, to which Fremy appropriates the term *Peruvine*.



The *resin* of Peru balsam is gradually formed, according to Fremy, by the hydration of cinnaméine, the formula of the perfect resin being  $C_{54}H_{30}O_{12} = C_{54}H_{26}O_8 + 4HO$ . (See also PLANTAMOUR, in reference to this subject, *Ann. der Pharm.*, xxvii. 329, and xxx. 341; and *Repertoire de Chimie*, 2 Sér., i. 77.)

TOLU BALSAM is the produce of *Myrospermum Toluiferum*, a tree growing on the mountains of Tolu and Turbaco, and on the banks of the Magdalena, between Garapatas and Monpox. (PEREIRA.) It exudes during the heat of the day from incisions in the bark, and is imported chiefly by way of New York and Jamaica, generally in tin canisters, but sometimes in earthen crocks, and in calabashes. When first brought over it is soft and tenacious, but gradually hardens; it is translucent, brown, very fragrant, and has a slightly sweet taste, softening between the teeth. When heated, it fuses and takes fire, diffusing an agreeable odor. The components of Tolu balsam are, according to Fremy, the same as those of Peru balsam; namely cinnaméine, cinnamic acid, and resin. These balsams, he observes, only differ in their degree of organization, and especially by the facility with which Tolu balsam becomes resinified. (*Ann. Ch. et Ph.*, Lxx. 203.) Hatchett, (*Phil. Trans.*, 1806,) Deville, and others, have also obtained a large proportion of benzoic acid from this balsam.

By the dry distillation of Tolu balsam, Muspratt and Hofmann (*Mem. Chem. Soc.*, ii. 372) obtained a large quantity of benzoic, mixed with a little cinnamic acid, and a yellow liquid, which, according to Deville, is a mixture of *toluole* and benzoic ether. By redistilling this liquid, so as only to collect the portions which pass over between  $265^{\circ}$  and  $285^{\circ}$ , a distillate was obtained, which, when deprived of benzoic acid by distillation with solid caustic potassa, possessed the properties ascribed by Deville (*Ann. Ch. et Ph.*, 3ème Sér., iii. 151) to toluole.

*Toluole*,  $C_{14}H_8$ , (inappropriately denominated *benzoène* by Deville) is a colorless limpid liquid, of the odor of benzine, volatile without residue, and boiling at  $226^{\circ}$ . The density of its vapor is 3.246. When toluole is acted on by concentrated nitric acid, and water afterwards



added, an oily fluid is obtained, which is *nitrotoluide*, =  $C_{14}H_7NO_4$ . By the action of sulphuret of ammonium upon nitrotoluide, Muspratt and Hofmann obtained a yellow oil, which gradually solidified into a crystalline mass. To this substance, which acts as an *organic base*, they have given the name of *Toluidine*. Their details respecting the method of its preparation are not sufficiently minute to admit of an intelligible abstract, so that I must refer to the original memoir, above quoted, for the mode of obtaining it. Toluidine is composed of

|                |    |     |     |     |        |                          |
|----------------|----|-----|-----|-----|--------|--------------------------|
|                |    |     |     |     |        | Muspratt<br>and Hofmann. |
| Carbon .....   | 14 | ... | 84  | ... | 78.50  | 78.53                    |
| Hydrogen ..... | 9  | ... | 9   | ... | 8.41   | 8.61                     |
| Nitrogen ..... | 1  | ... | 14  | ... | 13.09  | 12.86                    |
| <hr/>          |    |     |     |     |        |                          |
| Toluidine..... | 1  |     | 107 |     | 100.00 | 100.00                   |

Toluidine crystallizes from its hot solution in aqueous alcohol, in large broad plates. It is soluble in pyroxylic spirit, sulphuret of carbon, and the fat and volatile oils, with the same facility as in alcohol. It is very sparingly soluble in water. It has a vinous aromatic smell, and burning taste; it has no action upon turmeric, but it changes red dahlia paper to green. With nitric acid it produces a fine scarlet color, whereas aniline so treated assumes a blue tinge. The extraordinary crystalline tendency which distinguishes the salts of aniline, belongs also to those of toluidine. Its alcoholic solution almost immediately solidifies when mixed with an acid. Its salts are inodorous, and, with the exception of the platinum and palladium compounds, are colorless. The formula of the *sulphate of toluidine* is  $C_{14}H_9N + SO_3 + HO$ ; and that of the *hydrochlorate*,  $C_{14}H_9N + HCl$ .

STORAX BALSAM. The *Styrax officinalis* is a small tree growing in the Levant, Palestine, Syria, and Greece, and cultivated in the southern parts of Europe. The balsam exudes from incisions through the bark, and when somewhat hardened, constitutes one or more of the balsamic substances known in the drug trade under the name of *Storax*. The substances thus denominated are very numerous, and of variable character and composition; they are for the most part artificial compounds, perfectly unlike any of the genuine varieties. Real storax is extremely rare; it occurs in compact masses, of a very fragrant odor, and of a rich brown color, interspersed with white tears, whence the name *amygdaloid styrax*. It was formerly imported, enveloped in a monocotyledonous leaf, under the name of *cane* or *reed styrax* (*Styrax calamita*.) In the drug market two substances are generally met with, bearing the name of storax; one of them is called *styrax liquidus*; it is usually of a black, brown, or grey color, and generally has a disagreeable odor, more resembling that of coal-tar than of the balsam. The other is usually labelled *styrax calamita*, and is a black, brown, or purplish article, either pulverulent or granular, or in the form of agglutinated lumps. Some of it is said to consist of pulverized rotten wood, imbued with a little liquid storax; some of it appears to be fine sawdust, impregnated either with coal-tar, or something analogous, and not bearing the remotest analogy to anything which can be supposed to be genuine

storax. Blyth and Hofmann describe the material which they employed for the preparation of *styrole* as the "common commercial liquid storax," of a dark-grey color, and soft consistence at usual temperatures, but hard and brittle at  $32^{\circ}$ . It had a highly aromatic odor, and was so rich in oil, that it could be pressed out with the fingers. Storax has been experimented upon by Bouillon-Lagrange (*Annales de Chimie*, xxvi.,) by Bonastre, (*Journ. de Pharm.*, 1827, xiii. 149,) and by Simon, (*Ann. der Pharm.*, xxxi. 265.) Reinsch also has analyzed three varieties of storax, and finds them composed of resins of different degrees of solubility, together with gummy and extractive matter, a little benzoic (cinnamic?) acid, and a trace of volatile oil. *Styrole*, the volatile oil or hydrocarbon, obtained by Blyth and Hofmann, by distilling "liquid storax," and having the formula  $C_{16}H_8$ , has been above noticed, (p. 1543.) By repeatedly distilling a mixture of styrole and nitric acid, Simon, and afterwards Blyth and Hofmann, converted it into an acrid volatile body, which they term *nitrostyrole*, and to which they assign the formula  $C_{16}H_7NO_4$ .

## FOSSIL RESINS. BITUMENS. ASPHALTUM.

FOSSIL RESINS. AMBER, ( $C_{40}H_{32}O_4$ ), which is the principal of these substances, has already been described (p. 1391) as the source of *succinic acid*. A very pure, transparent, pale specimen of amber, was analyzed by Schrötter, (*Poggend. Ann.*, Lix. 64,) who found it to consist of

|                |    |     |     |     |        | Schrötter. |
|----------------|----|-----|-----|-----|--------|------------|
| Carbon .....   | 40 | ... | 240 | ... | 79.27  | 78.82      |
| Hydrogen ..... | 32 | ... | 32  | ... | 9.93   | 10.22      |
| Oxygen .....   | 4  | ... | 32  | ... | 10.80  | 10.96      |
| <hr/>          |    |     |     |     |        | <hr/>      |
| Amber .....    | 1  |     | 304 |     | 100.00 | 100.00     |

Berzelius describes amber as containing a volatile oil and succinic acid, together with two resins soluble in alcohol and in ether, and a third insoluble substance, of a bituminous character; the latter is the leading ingredient of amber. By digesting finely-pulverized amber in ether, it takes up about 10 *per cent.* of soluble matter, forming a pale-yellow solution, which, when mixed with water, and distilled so as to separate the ether, leaves a soft *balsam*, which is probably the unaltered or original vegetable product from which the amber has taken its origin, and which has been preserved from change by being enveloped in, or blended with the hardened and changed portion. This balsam has the odor of amber, and remains soft and glutinous for a long time; and when heated with the water in the retort, after the ether has passed over, it yields a very small quantity of a volatile oil, and leaves a pale-yellow opaque resin, whilst the water upon which this resin floats, holds succinic acid in solution; showing that that acid pre-exists in the amber, and is not a product of its destructive distillation. The water which distils over with the volatile oil holds a portion of it in solution; it has an agreeable odor, and a warm, aromatic, and slightly pungent taste. The resin which remains after the separation of the volatile oil, is separable by alcohol of 0.84 sp. gr. into a soluble and insoluble resin.



The bituminous portion of the amber which is not soluble in ether, is also insoluble in alcohol, in fixed and volatile oils, and in alkaline solutions. It forms a light yellow powder, still possessing the leading properties of the original amber. Subjected to dry distillation, it yields a colorless empyreumatic oil, and fuses into a dark-brown mass, which, when further heated, is almost entirely converted into a brown empyreumatic oil, leaving only a small carbonaceous residue. If the operation be stopped as soon as the amber-bitumen is in fusion, a resinoid mass is obtained (*amber-colophony*), which is translucent, and easily reduced into a highly electric powder. It is in this state that amber is principally used for varnishes. Alcohol extracts from it a small quantity of a yellow resin, very sparingly soluble in alkali. The further properties of these resins are described at length by Berzelius. (*Lehrbuch*.)

**HIGHGATE RESIN.** This substance was found in the blue clay of Highgate hill, near London, during the attempt to run a tunnel through it in 1813; it occurred in amorphous translucent pieces, of a brown color, and exteriorly smooth, as if rolled in water; harder and less brittle than resin, but softer than copal: of a resinous and aromatic odor when rubbed, and especially when heated. It is fusible, and may be rendered as fluid as water, without change of color. When in lumps, it is insoluble in water, alcohol, alkalis, and acetic acid; but ether renders it opaque, white, and tender, and dissolves a portion of it, which it deposits when mixed with water. Nitric acid partly dissolves, and partly converts it into a reddish substance; water precipitates the dissolved portion in the form of bitter white flocks. Sulphuric acid readily chars it when aided by heat. When in fine powder, a small portion of it is taken up by alcohol. (*Annals of Philos.*, ii. 9; THOMSON'S *Veg. Chem.*, p. 550.)

**RETINITE. RETINASPALTUM.** This substance was first noticed by Dr. Miller in the strata of bituminous wood (called *Bovey coal*) found at Bovey in Devonshire. (*Phil. Trans.*, 1760, vol. li., p. 534.) He states, that "amongst the clay, but adhering to the coal, are found lumps of a bright yellow *loam*, extremely light, and so saturated with petroleum, that they burn like sealing-wax, emitting a very agreeable and aromatic scent." It was afterwards described and analyzed by Hatchett, (*Phil. Trans.*, 1804, p. 385.) It is of a brown color, brittle, has an imperfectly conchoidal fracture, and a specific gravity = 1.135. When placed on a heated iron it melts, smokes, burns with a bright flame, and yields a fragrant odor. The fused mass, when cold, is black, brittle, and has a glossy fracture. It is to a great extent soluble in alcohol, which takes up 55 *per cent.* of a resinous substance, and leaves 41 *per cent.* of asphaltum, with a small proportion of earthy matter.

A retinite from the brown-coal of Halle has also been examined by Bucholz, (*Schweigger's Journ.*, i. 290,) of which 91 *per cent.* was soluble in alcohol. Another specimen, analyzed by Schrötter, (*Poggend. Ann.*, lix. 61,) yielded only 9 *per cent.* of resin: he represents its ultimate composition as  $C_{24}H_{18}O_2$ . In some specimens of Staffordshire coal I have found retinite in small detached nodules; and by digesting the

common varieties of pit-coal in ether, more or less of the same, or a similar product, may generally be obtained. Johnston applies the term *Retinic acid* to the substance extracted from the lignites of Bovey, by alcohol, and represents it by the formula  $C_{21}H_{14}O_3$ .

**TURF-RESIN.** Mulder has ascertained the presence of several resins in the turfs of Holland, and finds them differ in the light, or upper, and in the dense, or lower turf layers. He has assigned multitudinous formulæ to their several varieties. (*Revue Scientif.*, ii., 45; *Erdmann and Marchand's Journ.*, xxii. 44. See also LÖWIG, *Chem. der Org. verbind.*, ii. 1131.) Forchammer has also recognised several resinous substances in the ligneous remains of the turf-districts of Denmark. Some of them are crystallizable substances, such as *Tekoretine*, *Phylloretine*, and *Xyloretine*. *Boloretine*, which he also finds in the fallen leaves of fir-trees, especially after they have lain for some months upon the ground, is not crystallizable. (*Ann. der Pharm.*, xli. 39.) Bromeis found a resinoid substance, which he calls *Fichtelite*, upon the branches of a fir-tree, well preserved in the dry turf of Redwitz in the Fichtelgebirge, (pine-woods.) It proved to be a hydrocarbon  $= C_{20}H_{15}$ ; hence probably derived from oil of turpentine  $= C_{20}H_{16}$ . This substance is crystallizable, lighter than water, fusible at  $115^{\circ}$ , and volatile without decomposition. (*Ann. der Pharm.*, xxxvii. 304.)

**FOSSIL WAX. FOSSIL TALLOW.** These and other terms have been applied to certain fossile products, having more or less of the characters of wax or stearine. A substance of this kind described by Magnus, and found near Slamick in Moldavia, (*Ann. Ch. et Ph.*, lv. 215,) has been designated *Ozokerite*; it is said to contain no oxygen, and closely to correspond with the formula  $C_{16}H_{16}$ . It occurs in masses up to 100 pounds in weight, in a stratum of bituminous schistus. Malaguti (*Comptes rendus*, iv. 410,) has also examined it. It has a somewhat lamellar and fibrous structure; its fracture is conchoidal, and presents a pearly lustre; in thin layers it is translucent and pale-brown; it is a little harder than bees'-wax, and fuses between  $165^{\circ}$  and  $175^{\circ}$ . Its sp. gr. is 0.953; its odor is slightly that of petroleum; it becomes electric by friction. It is only partially soluble in alcohol and in ether, but readily soluble in oil of turpentine, naphtha, and fat oils. Its solutions are all brown by transmitted, but green by reflected light. It burns without much smoke, and is decomposed by dry distillation, one of its products being a waxy substance  $= C_{16}H_{16}$  (?) nearly insoluble in cold ether, but very soluble in boiling ether, and in boiling absolute alcohol; these solutions let the wax fall on cooling. There is also obtained along with this wax, an oily product, soluble in cold ether, which at low temperatures deposits paraffine.

Another substance of this class occurs in the argillaceous iron ore of Merthyr, in Glamorganshire. Conybeare, who first described it, distinguished by the name of *Hatchetine*, "in reference to the eminent chemist, to whom we are indebted for the most valuable contributions towards the history and analysis of this class of natural substances." (*Ann. of Phil.*, 2nd Ser., i. 136, Feb., 1821.) It is of a yellowish or greenish tint; its texture is sometimes flaky, like spermaceti, sometimes granular, like that of bees'-wax; it is translucent, soft like tallow, inodorous, and



fusible below  $170^{\circ}$ ; its sp. gr. is 0.93. It is found filling small contemporaneous veins in the iron-stone, lined with calcareous spar, and with the small rock-crystals called *Merthyr diamonds*. It is collected and preserved by the miners, who use it as a salve for burns and bruises. This species of *Mineral adipocire* has also been found in the coal strata of Newcastle and elsewhere. A substance much resembling it occurs in the beds of brown coal at Uznach, near Zurich, in Switzerland, where it was first observed by Koenlein. (*Poggend. Ann.*, xii. 336.) It resembles talc in appearance, and is soft, greasy, and very light. The terms *Scheererite* and *Koenleinite* have been applied to it by mineralogical nomenclaturists. From the analysis of Macaire-Prinsep, this substance may be regarded as  $C_{32}H_{16}$ . The substance designated by Johnston *Middletonite*, (from Middleton, near Leeds, where it occurs in the coal strata,) also appears to belong to this class: its ultimate elements are  $C_{86.5}, H_8, O_{5.5}$ , per cent. It is hard, brittle, of a brownish-red color, inodorous, tasteless, and blackens by exposure to air. It burns like a resin, and leaves a bulky coal, which consumes without residue.

*Idrialine*, mentioned among the *hydrocarbons* (p. 492,) as having been analyzed by Dumas, has also been examined by Schrötter, and by Boedeker; the latter chemist assigns to it the formula  $C_{42}H_{14}O$ ; he found in it about 3 per cent. of oxygen. (*Löwig. Chem. der Org. verb.*, ii. 905.)

**PETROLEUM.** *Rock Oil. Mineral Tar. Barbadoes Tar.* This liquid appears to be naphtha holding asphaltum, or perhaps other bituminous products, in solution. *Natural naphtha* has been already mentioned (p. 488), and is often accompanied by petroleum.

*Petroleum* is of a dark-brown color, translucent, viscid, of a strong bituminous odor, and a pungent taste. It is very slightly soluble in alcohol, which however acquires its odor and color. Its sp. gr. is about 0.878, but liable to much variation, as are also its other properties, dependent upon its variable composition. It is found in various countries of Europe, and in the West Indies; but no country produces it so abundantly as the Birman Empire in Asia. "The town of Rainanghong is the centre of a small district in which there are some hundred petroleum-wells in full activity. The district in which they are situated consists of a sandy loam, resting upon alternate strata of sandstone and indurated clay; under these is a layer of pale-blue argillaceous schistus, impregnated with petroleum, of considerable thickness, and resting upon coal. The petroleum flows into the well when it is sunk a few feet into the schistus, and when it begins to fail, the well is deepened. It is remarkable that no water ever penetrates into these wells. The annual quantity of petroleum produced by the district exceeds 400,000 hogsheads." (Cox, *Asiatic Researches*, vi. See also AIKIN'S *Dict. of Chem. and Miner.* Art. *Bitumen*.) "The uses of petroleum where it abounds, are very important; it serves the lower classes instead of oil for lamps, and when mixed with earth or ashes it answers the purpose of fuel. A composition of petroleum and resin is an excellent material for covering wood-work, and paying the bottoms of ships and boats, as it protects the timber from the attacks of insects and worms. When rectified by distillation, it affords naphtha."

ASPHALTUM. *Jew's Pitch.* *Mineral Pitch.* *Maltha.* This indurated bituminous substance occurs in considerable quantity on the shores of the Dead Sea, in Judea; it is found in detached pieces upon the banks, and floating upon the surface; hence it was called the *Asphaltic Lake*. It abounds also in the West Indian Islands of Barbadoes and Trinidad. In the latter island there is a remarkable plain, about three miles in circumference, called the *Tar-lake*, and consisting entirely of a stratum of asphaltum. Its consistence and general appearance somewhat resemble that of coal; it easily breaks into small cellular glossy fragments. The thickness of this stratum has not been determined, but when cut into, it is softer, and the cells contain petroleum. It does not easily burn, but a gentle heat renders it ductile, and when mixed with grease, or common pitch, it is used for paying the bottoms of ships, and is said to protect them from *teredines*. (ANDERSON, *Phil. Trans.*, LXXIX. 65.) There is a thick bed of asphaltum at Arlona, in Albania; it constituted a leading ingredient in the celebrated Greek Fire of the middle ages. It also occurs at Coxitambo, near Cuenca, in South America.

The varieties of asphaltum vary much in purity, in consequence of the admixture of variable proportions of different earthy substances. The purer kinds are almost black, or dark brown, of a resinous appearance and conchoidal fracture, opaque, brittle, and do not soil the fingers. When rubbed it has a slightly bituminous odor. Its specific gravity varies with its purity, that of the purest varieties being from about 1 to 1.10. The specific gravity of the asphaltum of Coxitambo, which Boussingault refers to as the *type* of these substances, is 1.08; it has the fracture and appearance of obsidian. When laid upon a hot iron it burns with a yellow smoky flame, softening and swelling up, rather than entering into fusion, and there remains a light spongy coal, which burns away, leaving a little ash. Subjected to dry distillation, it yields a brown oil, a little ammoniacal water, and inflammable gases, and leaves about one-third of its weight of carbon. Asphalt is insoluble in water. Absolute alcohol takes from it about 5 *per cent.* of a yellow resin; and ether dissolves it to the extent of about 70 *per cent.*, leaving, on evaporation, a blackish brown substance, very soluble in naphtha and in oils. That portion of asphalt which is insoluble in alcohol and difficultly soluble in ether, has been designated by Boussingault *Asphaltene*, (*Ann. Ch. et Ph.*, LXIV. 148, and LXIII. 442;) he ascribes to it the formula  $C_{40}H_{32}O_6$ , which, however, is quite inconsistent with the analytical results given in his second memoir, in which he represents the *per centage* composition of the asphalt of Coxitambo (Peru) as =  $C_{88.70}, H_{9.68}, O \ \& \ N, 1.62$ .

The bitumens of Bechelbroun (dept. du Bas-Rhin), of Seyssel on the Rhone (dept. de l'Ain), of Pont du Chateau in Auvergne, and of Lobsann (Bas-Rhin), are soft or glutinous, and yield no volatile product when heated in a retort up to  $212^{\circ}$ ; they therefore contain no naphtha. They are usually purified by boiling them with water, which separates the sand and earthy matters, and the bitumen then floats upon the boiling water, and is skimmed off. When thus purified, and heated to  $445^{\circ}$  in an oil bath, drops of an oily hydrocarbon distil over, which Boussingault distinguishes by the term *Petrolene*. When the bitumen of Bechelbroun is distilled with water, the vapor carries the petrolene over with it.

*Petrolene* is pale yellow, has little taste, and a bituminous odor. At



68° its sp. gr. is 0·891. It burns with a fuliginous flame. It boils at about 538°. It is very slightly soluble in alcohol, but more abundantly in ether. The density of its vapor is 9·415, which is double that of terpentine vapor. The ratio of the carbon to the hydrogen in petrolene is the same as in oil of terpentine, lemon, &c., so that it may be represented as constituted of

|                 |    |     |     |     |        |     |     |
|-----------------|----|-----|-----|-----|--------|-----|-----|
| Boussingault.   |    |     |     |     |        |     |     |
| Carbon .....    | 20 | ... | 120 | ... | 88·23  | ... | 88  |
| Hydrogen .....  | 16 | ... | 16  | ... | 11·77  | ... | 12  |
| <hr/>           |    |     |     |     |        |     |     |
| Petrolene ..... | 1  |     | 136 |     | 100·00 |     | 100 |

BITUMINOUS SCHISTUS. The products of the distillation of this substance have been examined by Laurent, (*Ann. Ch. et Ph.*, liv. 392, and LXIV. 321,) and in reference to their useful applications, by Selligie. (DUMAS, *Chim. app. aux Arts*, vii. 390.) These schisti are abundant in various parts of the world; they are more or less combustible, and when subjected to dry distillation they afford a considerable quantity of inflammable gas, water, and oil, and leave a mixture of carbon and earthy matters, constituting a species of porous coke, which has been used as a decoloring material. The following results of the decomposition of two samples of this schistus are given by Boussingault and Dumas:

|                         |    |       |       |
|-------------------------|----|-------|-------|
| Inflammable gases ..... | 14 | ..... | 9·8   |
| Oil .....               | 20 | ..... | 14·5  |
| Water, &c. ....         | 8  | ..... | 6·4   |
| Charcoal .....          | 19 | ..... | 7·7   |
| Earthy substances ..... | 39 | ..... | 61·6  |
| <hr/>                   |    |       |       |
|                         |    | 100   | 100·0 |

When the oil is distilled, it affords products differing in volatility: if, after two-thirds have passed over, the receiver be changed, the product is of a greenish or brownish color, and its boiling-point is above 500°; when cooled down to 32°, it deposits a crystalline substance having the characters of paraffine (p. 1212.) The more volatile portions of this oil, which first pass over, boil as low as at 140°, and from that to 212°. It has an empyreumatic odor a little like naphtha, and produces a greasy spot upon paper, which almost immediately evaporates. Laurent has described the properties of the portions of oil which pass over between 176° and 186°, between 240° and 255°, and between 300° and 340°. By acting upon the oil obtained between 180° and 300° by nitric acid, he obtained a white flocculent substance which he calls *ampelic acid*. By agitating that part of the oil which boils between 390° and 535°, with repeated portions of concentrated sulphuric acid, and then mixing it with about a twentieth part of an aqueous solution of caustic potassa, and leaving it at rest for a day, the liquor separates into two layers, of which the inferior aqueous portion is more bulky than the solution of potassa used. When this portion is shaken with dilute sulphuric acid, an oil separates upon the surface, soluble in 20 times its volume of warm water. When this aqueous solution is mixed with sulphuric acid, an oily matter separates which Laurent terms *Ampeline*, and which is remarkable as having the characters belonging to an oil, conjoined with solubility in water; it also dissolves, in all proportions, in alcohol and in ether. It is converted by boiling nitric acid into an

insoluble viscid substance, and oxalic acid. A solution of ampeline in 40 parts of water is singularly acted upon by the following reagents: a few drops of sulphuric or of nitric acid, even very dilute, separate the ampeline: potassa and ammonia render it slightly turbid at first, but by agitation, and heat, the liquor becomes clear: carbonate of ammonia renders it turbid; so also do carbonate of potassa and of soda, but with the latter it again clears when heated: the ampeline is separated by the addition of chloride of ammonium, chloride of sodium, and phosphate of soda. Subjected to distillation, ampeline is decomposed; water, and a light limpid oil pass over, and carbon remains in the retort: ampeline therefore contains oxygen. It differs from all known substances, but perhaps in its origin and properties it most nearly resembles kreasote. (LAURENT.)

WOOD-SOOT. This substance has been analyzed by Braconnot, (*Ann. Ch. et Ph.*, xxxi. 37.) Two kinds of soot are deposited in chimneys in which wood is burned, namely, one which is near the fire, and fused into glossy masses; the other, pulverulent, and found in the higher parts of the flue. The following details relate to the latter; it was collected at a medium height, and exclusively derived from wood.

When wood-soot is digested in water it tinges it yellow, and brown if heated, when the soot agglutinates in consequence of the softening of the resinoid matter which it contains. The aqueous solution contains combinations of the resinoid or pitchy matter with potassa, lime, and magnesia, together with sulphate of lime, chloride of potassium, acetate of ammonia, and traces of nitrates. When evaporated, it leaves a black extract, soluble in water, with the exception of a residue of brown gypsum. But the bulk of the soot consists of the pitchy resinoid, which, according to Braconnot, contains a peculiar substance, which he terms *Asboline* ( $\alpha\sigma\beta\omicron\lambda\eta$ , soot.) It is of a thick oily consistence, and when decomposed by dry distillation, yields ammonia. When heated in the air it burns like oil; it is lighter than, and very sparingly soluble in water: its alcoholic solution is not rendered turbid by dilution with water. The other substances contained in wood-soot will be seen in the following enumeration of its components; which, however, is useful rather as a qualitative than a quantitative analysis, inasmuch as the relative proportions of the specified substances must, at all events, be liable to great variation.

|   |       |
|---|-------|
| 1. Ulmine .....                                     | 30·20 |
| 2. Azotised extractive matter .....                 | 20·00 |
| 3. Asboline.....                                    | 0·50  |
| 4. Carbonate of lime with a trace of magnesia ..... | 14·66 |
| 5. Acetate of lime.....                             | 5·65  |
| 6. Sulphate of lime .....                           | 5·00  |
| 7. Chloride of potassium .....                      | 0·36  |
| 8. Phosphate of lime.....                           | 1·50  |
| 9. Acetate of potassa.....                          | 4·10  |
| 10. Acetate of ammonia .....                        | 0·20  |
| 11. Acetate of magnesia .....                       | 0·53  |
| 12. Silica .....                                    | 0·95  |
| 13. Water.....                                      | 12 50 |
| 14. Traces of oxide of iron .....                   | ...   |
| 15. Carbon .....                                    | 3·85  |

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 100·00



## CAOUTCHOUC. GUTTA PERCHA. ELASTIC BITUMEN.

CAOUTCHOUC. *Indian-Rubber. Gum Elastic.* This substance was first brought from America about the beginning of the last century, moulded into the shape of bottles and animals, and used for rubbing out the marks made upon paper by a black-lead pencil; but nothing was known of its history, till De la Condamine sent an account of it to the French Academy in 1736, describing it as the inspissated milky juice of a tree called by the natives *Hevee*. In the year 1751 Frisnau discovered the same tree in Cayenne. (*Mem. Paris*, 1751, p. 319.) Caoutchouc is now known to be the produce of several trees growing in South America, and also in the East Indies. The American Indian-rubber is said to be chiefly derived from the *Siphonia Caoutchouc* (*Jatropha elastica*, LINN.) and the *East-Indian* from *Urceola elastica*. A similar juice exudes from *Hevea Guianensis*, *Cecropia peltata*, *Ficus Indica*, *Castelleia elastica*, &c., and the poppy, the lettuce, some of the *Euphorbiums*, and other plants having viscid milky sap, seem also to contain it.

The juice of the Indian-rubber tree is sometimes sent in bottles to this country; it is usually pale-yellow and creamy, and contains more or less of deposited caoutchouc. Faraday describes it as having a sourish and slightly putrid odor, and a sp. gr. = 1.0117. When spread upon a solid body in thin layers, it forms an elastic deposit; it contains about 32 per cent. of caoutchouc, with a little albumen, wax, and gum, and a brown bitter azotized substance soluble both in water and alcohol. (*Journ. of Science*, xxi. 19.) When this juice is heated, the caoutchouc coagulates, and envelopes and mixes with the albumine. To obtain pure caoutchouc the fresh juice is well mixed with about 4 parts of water, and left for 24 hours, when the suspended caoutchouc collects upon the surface in the form of cream, and the fluid beneath is drawn off; the cream is then again washed and separated as before, and the operation repeated till nothing further is removed by water, when the finely-divided caoutchouc is separated from the water by adding a little salt, or acid, and is dried either upon porous tiles, or by gently heating it; and in proportion as the water evaporates, the particles form an adherent mass.

The general characters of this substance are well known. Its sp. gr. is about 0.925; it is a non-conductor of electricity. At very low temperatures it becomes to a certain extent hard, but never brittle; when boiled in water or in alcohol, it swells and softens, and is in that state comparatively easily acted upon by such substances as dissolve it. It burns readily with a smoky flame, exhales a peculiar odor, undergoing a kind of fusion. It is perfectly insoluble in water and in alcohol. Ether, when it has been washed so as to deprive it of alcohol, dissolves it, with the exception of sooty and albuminous impurities, and leaves it on evaporation, in its perfectly elastic state. This ethereal solution is precipitated by alcohol, and this is the best process for obtaining it in its milky form. It also dissolves in sulphuret of carbon. In cold naphtha caoutchouc swells up to as much as 30 times its original volume, forming a soft pasty mass, the greater part of which is taken up by the further addition of naphtha and the help of heat. On the evaporation of the naphtha, the caoutchouc long remains sticky, and the last por-

tions of the solvent are with great difficulty got rid of; the best mode of proceeding consists in exposing it to a current of steam. It also dissolves in the rectified empyreumatic oils of coal and of wood, and in oil of turpentine, of lavender, and sassafras, and when evaporated, they leave it in its elastic condition. The oil of turpentine distilled *per se* at a high temperature (see p. 1537) has the greatest solvent power over caoutchouc. It also is softened by and partly soluble in other volatile, and in many of the fixed oils, but it forms with them viscid and glutinous compounds, which never dry into an elastic state. A compound of this kind obtained by boiling 4 ounces of caoutchouc cut into shreds, in 2 lbs of linseed oil, till dissolved, and then passing it through a strainer, has been used for rendering boots water-tight. Nitric acid renders caoutchouc yellow, and when aided by heat, gradually dissolves and decomposes it. Water renders this nitric solution turbid and yellow. By sulphuric acid it is superficially charred, and when heated, acquires the consistence of turpentine, and sulphurous acid is evolved. The solutions of the caustic alkalis do not act upon caoutchouc, nor is it acted upon by chlorine or bromine. The ultimate components of caoutchouc are

|                  |   |      |    |      |        | Faraday.  |
|------------------|---|------|----|------|--------|-----------|
| Carbon .....     | 8 | .... | 48 | .... | 87.27  | .... 87.2 |
| Hydrogen .....   | 7 | .... | 7  | .... | 12.73  | .... 12.8 |
| <hr/>            |   |      |    |      |        |           |
| Caoutchouc ..... | 1 |      | 55 |      | 100.00 | 100.0     |

The almost innumerable applications of caoutchouc in various forms render even an abstract of the subject inadmissible here. Dumas, in his *Chimie appliquée aux Arts*, and Dr. Ure, in his *Dictionary of Arts*, &c., have each given an outline of these details. The late Mr. Macintosh, of Glasgow, was the first who successfully applied the solutions of caoutchouc to the manufacture of waterproof articles of clothing. A variety of elastic fabrics are also woven out of caoutchouc stretched into threads, and covered with cotton. The operations of cutting, grinding, and forming caoutchouc into blocks, which are afterwards sliced, and reduced to filaments of various degrees of tenuity, together with a variety of other curious forms and preparations of this article, are described by the authorities above quoted. The reader should also consult, in reference to it, the various processes detailed in the specifications of Hancock's patents. The facility with which two recently cut and perfectly clean surfaces of caoutchouc adhere, or as it were weld together, render it an invaluable article in the laboratory for the formation of short elastic tubes which are used as *connectors* for a variety of apparatus, in which separate pieces of glass tubing are thus joined together with flexible joints. They are prepared by wrapping a piece of sheet caoutchouc loosely over a glass tube or rod, and then cutting off the superfluous portion with a pair of sharp scissors: on carefully pressing the fresh-cut edges together, they cohere so as to form a perfect tube.

*Products of the dry distillation of Caoutchouc.* Common caoutchouc, and especially the whitish porous masses of it which frequently occur in commerce, yields, when heated, a considerable proportion of apparently hygrometric water, and this is succeeded by certain products arising from the action of the heat upon the albumine and azotized substances present. When these are decomposed, and the real products of the



destruction of the caoutchouc itself are formed, they chiefly consist of gaseous and liquid hydrocarbons, the latter, when duly condensed, amounting to as much as from 80 to 85 *per cent.* of the original pure caoutchouc. This volatile oil, first obtained by Messrs. Beale and Enderby, has, when purified, received the name of *Caoutchisine*. It has been particularly examined by Dalton (*Phil. Mag.*, 3rd Ser., ix. 479), Liebig, (*Ann. der Pharm.*, xvi. 6,) Himly, (*De Caoutchouc, ejusque distillationis siccae productis, &c.*, Göttingen, 1835,) and Bouchardat, (*Journ. de Pharm.*, xxiii.) Chevallier, Trommsdorff, and Gregory, have also experimented upon it.

*Caoutchisine*, like most similar products, is a mixture of hydrocarbons, which may to a certain extent be separated by graduated distillation. According to Himly, caoutchouc, when distilled, leaves charcoal, and yields about three-fourths of its weight of volatile oil, of a thick consistence and dark color. When this is re-distilled, a portion passes over between  $130^{\circ}$  and  $205^{\circ}$ , which may again be resolved, by distillation, into a portion which boils at  $90^{\circ}$ , and which is apparently identical with Faraday's *bicarburet of hydrogen* (p. 483,) and into a second portion, the boiling-point of which exceeds  $212^{\circ}$ , and principally fluctuates between  $300^{\circ}$  and  $600^{\circ}$ ; this portion also consists of hydrocarbons, in which the proportion of carbon is greatest when the boiling-point is highest. According to Bouchardat, the most volatile of the products of the distillation of purified caoutchousine is identical with Faraday's *quadrihydrocarbon* or *etherine* (p. 485.) Bouchardat has applied the term *Hevæene* to a liquid which he obtained by distilling rectified caoutchisine with water as long as any part of it passed over with the aqueous vapor, and then re-distilling the residue in an oil-bath.

*Hevæene* is a pale-yellow oil of a somewhat empyreumatic odor, and a pungent taste: it boils at about  $600^{\circ}$ ; its sp. gr. is 0.921. It does not congeal at a very low temperature; it burns with a bulky sooty flame. It is soluble in all proportions in absolute alcohol, ether, and fat and volatile oils; it contains 85.24 *per cent.* of carbon, and 14.76 of hydrogen. It is decomposed by boiling, and resolved into gaseous and liquid products, the latter of which have a lower boiling point. It rapidly absorbs chlorine, and hydrochloric acid is evolved. It acts similarly with iodine and bromine.

When hevæene is mixed with sulphuric acid, a thick tough mass is at first formed, from which a transparent oily fluid gradually oozes; when this fluid is again treated with sulphuric acid, and afterwards with potassa, and then distilled, a colorless neutral oil passes over, of an agreeable odor, and which boils at  $440^{\circ}$ . Hevæene is probably =  $C_{16}H_{16}$ .

The crude purified caoutchisine has been proposed as a solvent for caoutchouc, and is very effective; but it is too expensive for practical use, and its highly disagreeable, greasy, and penetrating odor, would alone render it almost unavailable.

*Sulphuretted Caoutchouc. Vulcanized Indian-Rubber.* Under these names a preparation of caoutchouc has lately been made known by Hancock and Brockedon, possessed of some very extraordinary properties, and applicable to a variety of new and useful purposes. It is obtained by different processes, one of which consists in submitting the Indian-

rubber to the action of bisulphuret of carbon mixed with chloride of sulphur; but by this operation the article is not penetrated to any depth, so that it is inapplicable when thick masses are to be converted. In such cases the Indian-rubber is either immersed in a bath of melted sulphur, where it gradually acquires somewhat of the appearance and consistence of horn; or it is reduced, by some of the usual processes, to a state of fine division, and then thoroughly kneaded with finely-pulverized sulphur, and exposed to a temperature of  $190^{\circ}$ . Another, and perhaps the most applicable process for general purposes, consists in digesting or dissolving the Indian-rubber in naphtha or in oil of turpentine previously saturated with sulphur.

The peculiarities of Indian-rubber thus treated, are, 1. That it remains perfectly flexible and elastic at all temperatures; whereas, in its ordinary state, it becomes rigid at  $40^{\circ}$  and below. 2. Vulcanized caoutchouc is no longer soluble in those liquids which take it up in its ordinary state; when immersed, for instance, in naphtha, turpentine oil, or sulphuret of carbon, it increases in bulk, and in some cases acquires a peculiar brittleness, but it does not gelatinize and dissolve. 3. It sustains a comparatively high temperature without softening, as is the case with the ordinary article: according to Brockedon, it is not affected by a heat short of the vulcanizing point. 4. It acquires extraordinary powers of resisting compression; and when substances are thrust through it, they leave scarcely a perceptible rent. This form of caoutchouc has already been applied to many useful purposes, and promises to become of much more extensive importance. (BROCKEDON. *Chem. Gaz.*, 1847, p. 246.)

GUTTA PERCHA. This substance appears to have been first brought into notice by Dr. Montgomerie. (*Mechanics' Magazine*, October, 1846.) It is the produce of a large forest tree, (*Isonandra Gutta*, Nat. Ord. *Sapotaceæ*. HOOKER, *Lond. Journ. Bot.*, 1847, and *Pharm. Journ.*, vii. 180,) growing in the mountains of Singapore, and in the forests of Johore, at the extremity of the Malayan Peninsula, and in Borneo; it is also supposed to abound on the clusters of islands to the south of Singapore. The gutta percha appears to separate from the juice or sap of the tree, in the same way as Indian-rubber; its general properties in regard to solvents, and to the products of destructive distillation, resemble those of caoutchouc. At common temperatures gutta percha is hard, and very tough and unyielding, but when immersed in boiling water, it softens, so as to admit of being beaten into a mass and moulded into any requisite shape, and again hardens as before, on cooling. In thin films it has a pale-yellow or pinkish tinge, but generally occurs in brown or blackish lumps, or masses, of a somewhat mottled appearance upon the cut surface, and translucent. When softened, it may be stretched into slips, which do not recover their former bulk when the force is withdrawn, but on cooling have a certain degree of leathery elasticity. When heated to about  $250^{\circ}$ , it undergoes a kind of fusion, and remains viscid when cold. It burns with a strong yellow smoky flame. It is said to be obtainable in very large quantities, but from the destructive mode hitherto pursued by the natives in obtaining it, there appears to be some risk of the extermination of the trees. Gutta percha has already been applied to the manufacture of cements, architectural ornaments, book-binding,



soles of boots and shoes, picture-frames, bottles and tubes, &c., and combined with caoutchouc and other things, it is used for elastic bands employed in driving machinery, for saddles, cushions, walking-sticks, &c.

**ELASTIC BITUMEN.** *Mineral Caoutchouc.* This substance was originally found in a deserted mine near Castleton in Derbyshire, and noticed by Dr. Lister, (*Phil. Trans.*, 1673.) It was first accurately described by Hatchett in 1816 (*Linnæan Transactions*, iv. 146.) but had been previously examined by Delametherie, (*Journ. de Phys.*, xxxi. 312,) and by Klaproth (*Beiträge*, iii. 109.) It was afterwards discovered in France, in Switzerland, and in the Island of Zante. It is of a brown color, soft, flexible, and elastic: its sp. gr. varies between 0·9 and 1·2. It has a slight but peculiar odor, and some of the varieties are extremely like caoutchouc. When boiled in water a small portion of volatile matter separates, and it acquires a paler color. It is insoluble in alcohol and ether, and in alkalis and acids, but is acted upon by naphtha much in the same way as caoutchouc. Some of the varieties, when digested in alcohol and in ether, yield as much as 18 *per cent.* of soluble resinoid, or retinasphaltic matter. According to Johnston, purified elastic bitumen is a hydrocarbon containing from 83 to 86 *per cent.* of carbon.

#### § XIV. CHEMICAL BOTANY.

THIS section includes references to a number of substances which it has not been thought necessary to mention elsewhere in detail, and to the results of analyses, which, although elsewhere adverted to, have not been specifically quoted. The articles are arranged alphabetically, according to the usually accepted botanical names of the plants whence they are derived.

*Achillea millefolia*, contains a peculiar bitter principle, *Achilleine*, united to a peculiar acid, *Achilleic acid*. (ZANON, *Ann. der Pharm.*, lviii. 21. *Chem. Gaz.*, Jan. 1847.)

*Aconitum napellus*. The leaves of this, and other species of *monkshood*, contain the poisonous alkaloid which has already been described (p. 1459). Its paralyzing power upon the organs of taste may be perceived by chewing a leaf of the plant; it produces a biting sensation upon the tongue, and *taste* is impaired for hours afterwards. Bucholz found in the fresh leaves 83·75 *per cent.* water; the residue washed with water left 15 *per cent.* of woody fibre. On heating the expressed juice, a green and albuminous fecula subsided, amounting, with a little wax, to 5·0. Alcohol abstracts from the inspissated juice of aconite a brown extractive, of a bitter, sourish, saline, and acrid flavor. The part insoluble in alcohol yielded to water 3·75 of gum, and left 1·0 of malate and citrate of lime.

*Æsculus hippocastanum*. The bark of the *horse-chestnut* has been partially examined by Henry. (*Ann. de Ch.*, lxxvii.) It appears to contain scarcely any resin; water and diluted alcohol dissolve nearly the whole of its soluble contents, which are chiefly extractive and mucilage. Tincture of galls does not render its infusion turbid; it does not contain

an alkaloid. According to Pelletier and Caventou, this bark contains a green fixed oil, a red resin, a red extract, a yellow bitter extract, tannine, gum, and a free acid. According to Jonas, and to Trommsdorff, (*Ann. der Pharm.*, xiv. and xv.) when the greater part of the alcohol is distilled from a strong alcoholic infusion of horse-chestnut bark, it deposits a peculiar principle which they term *Æsculine*, and which, when purified by solution in, and deposition from a boiling mixture of 1 part of ether and 5 of alcohol, is a white crystalline powder, inodorous, slightly bitter, and soluble in 12·6 parts of boiling water, which solution concretes on cooling into a bulky white mass. When a mere trace of æsculine is dissolved in spring water, it communicates to it a blue opalescence. The formula assigned to æsculine is  $C_{16}H_9O_{10}$ .

*Æthusa cynapium*. According to Ficinus, a crystallizable alkaloid, *Cynapine* (or *Æthusine*?) may be extracted from this plant. (*Magazin für Pharm.*, xx. 357.)

*Agaricus muscarius*, &c. By expressing the juice of these fungi, heating it to coagulate the albumine, precipitating the filtered liquor by basic acetate of lead, decomposing the precipitate by sulphuretted hydrogen, evaporating the filtrate to dryness, and digesting it in ether, Letellier obtained an uncrystallizable inodorous substance to which the poisonous properties of the fungi have been ascribed: it has been termed *Aminiline*.

The substances found in all *fungi* are a crystalline and a butyraceous fat, albumine, sugar, two azotized bodies, one of which is only soluble in water, and the other in water and alcohol, and salts of potassa and of ammonia, with fungic, boletic, phosphoric, and sometimes acetic acid, fungine (a form of lignine), and water. Many contain gum and mucilage.

When bruised fungi are digested in water, they yield an *extract*, from which alcohol abstracts sugar and an azotized substance, separable by a little alcohol, which dissolves the former and leaves the latter. This azotized substance yields a brown solution with water, which, when evaporated leaves it in the form of a brown extract, smelling, when heated, like roasted meat, evolving ammonia when distilled, and in most respects resembling the animal extractive called *osmazome*. The portion of the extract insoluble in alcohol, dissolves in water, with the exception of a little albumine; it also dissolves in dilute alcohol: it does not gelatinize, and when destructively distilled, yields carbonate of ammonia. The insoluble portion of the fungi which remains after digestion in water, digested in alcohol, yields stearine and elaine, and a little resin.

*Amomum grana paradisi*. The seeds of this plant, called *grains of paradise*, or *guinea grains*, are very hot and peppery: they contain a pungent volatile oil, and an acrid resin. (WILLERT. *Berzelius' Lehrbuch*.)

*Amomum cardamomum*. (*Elettaria Cardamomum*.) *Cardamom seeds* yield of essential oil 4·6; fixed oil, 10·4; salts, coloring matter, and an azotised principle, 4·7; fecula, 3·0; woody fibre, 77·3. (TROMMSDORFF, *Journ. de Chim. Med.*, 2nd Sér. i. 196.)

*Amomum zinziber*. (*Zingiber officinale*.) *Ginger root* contains 1·56 volatile oil, 3·6 acrid resin, 10·5 acrid and sourish extractive, 12·5 gum, 19·75 starch? 8·3 mucilage, 26 extractive, 8 lignine; remainder, water



and loss. (BUCHOLZ.) It has also been examined by Morin, (*Journ. de Pharm.*, ix., 253.) The *resin* appears to be the principal source of the acrimony of ginger, but the volatile oil is also very pungent.

*Amygdalus communis*. Sweet almonds contain 54 oil, 6 sugar, 3 gum, 24 emulsine, 12 lignine, water, and loss. (BOULLAY.) Bitter almonds contain the same principles, and *amygdaline*, above described, p. 1375. The bitter-almond-cake, which remains after the expression of the fixed oil, yields an average produce of 9 oz. of *volatile oil* from the hundred-weight, but much depends upon the mode of distillation.

*Andropogon Ivaracusa*. An oil brought into this country under the name of *East Indian grass oil*, is said to be derived from the above plant. It has a peculiar fragrant odor, and has been analyzed by Stenhouse. (*Mem. Chem. Soc.*, ii. 122.) Hatchett, in an Essay upon this oil, (privately printed,) endeavours to show, that it is the *oil of spikenard* of Scripture. According to Hamilton the *lemon-grass* of the West Indies is probably the same plant. (*Pharm. Journ.*, viii. 369.)

*Angelica officinalis*. The root of this plant contains peculiar acids, described by Buchner, Meyer, and Zenner. (*Ann. der Pharm.* LV. 317.) See also Kopff, and Reinsch, (*Chem. Gaz.*, June 1846,) and *valeric acid*, p. 1553.

*Anthemis nobilis*. Chamomile flowers yield, on distillation, a blue or green essential oil, which becomes yellow when kept. 100 lbs. of the dried flowers yield, upon an average, 2 lbs. 12 oz. of oil, and 3lbs. 4 oz. of *pharmaceutical extract*.

*Anthemis pyrethrum*. Pellitory of Spain. The stimulating power of this root upon the salivary glands is due to its soft resin. It contains traces of volatile oil, soft resin 5, yellow extractive 14, gum 11, inuline 33, lignine 35. (GAUTIER, *Journ. de Pharm.*, iv. 50.) It has also been examined by Parisel, (*ibid.* xix. 251) and by Koene. (*Ann. Ch. et Ph.*, lix. 328.)

*Apium petroselinum*. When parsley is boiled in water, and the boiling liquor strained, it yields a jelly on cooling, resembling pectic acid. When washed with cold water it is neutral, insipid, and inodorous: its solution is peculiarly characterized by affording a blood-red color on the addition of protosulphate of iron. Braconnot, who terms this substance *Apiine*, has further described its properties. (*Ann. Ch. et Ph.*, Oct., 1843.)

*Arbutus uva ursi*. The leaves of the *whortle-berry* are very rich in tannine, and might be much more employed than they are in tanning and dyeing; they might be abundantly imported from the north of Europe. At present they are only used in medicine as an astringent and tonic, especially in affections of the urinary passages. Löwig describes a peculiar crystallizable bitter principle as contained in these leaves, under the name of *Arbutine*.

*Aristolochia serpentaria*. The root contains volatile oil 0·5, yellow soft resin 2·85, extractive 1·70, saponaceous gum 18·10, lignine 62·4, water and loss 14·5. (BUCHOLZ.) According to Chevallier, (*Journ. de Pharm.*, vi. 565,) the virtues of this root are referable to a distinct principle, which he terms *Aristolochine*.

*Arnica montana*. The flowers contain an acrid extractive (cytisine?)

and resin, to which their medicinal virtues are ascribed: they also yield a volatile oil, tannine, gallic acid, gum, &c. (CHEVALLIER and LASSAIGNE, *Journ. de Pharm.*, v. 248.) Dr. A. T. Thomson is of opinion that strychnia exists in this plant. (*Lond. Disp.*, 9th Edit., p. 213.)

*Artemisia absinthium*. Wormwood has not been examined by modern chemists. According to Dörffurt, dry wormwood yields about 1 per cent. of volatile oil, 8·5 to 9 of green resin, 25 to 30 of gummy extract, which, when burned, leaves 11·5 per cent. of the original weight of the dried herb, of ashes, two-thirds of which are *carbonate of potassa*: hence the term *salt of wormwood* applied to that salt. A peculiar bitter substance has been obtained from this plant by Caventou, *Absynthine*, (*Journ. de Pharm.*, xiv. 577; see also Mein, *Ann. der Pharm.*, viii. 61.)

*Artemisia santonica*. The buds, or broken peduncles of this plant, are said to constitute the article known in pharmacy under the name of *Semen santonicum*, *Semen cinæ*, *Semen contra*, &c. They come from the Levant. Trommsdorf has described a well-defined crystalline substance obtained from them, under the name of *Santonine*, (*Ann. der Pharm.*, xi. 190,) and which has been analyzed by Liebig and Ettling, (*Ibid.*, 208.) It forms white prisms, very little soluble in water, soluble in 43 of cold, and in 2·7 of boiling alcohol. It combines with bases in the manner of an acid. Its analysis leads to the formula  $C_{30}H_{18}O_5$ .

*Asclepias vincetoxicum*. The roots contain an emetic principle, which has been described by Feneulle under the name of *Asclepine*.

*Asparagus officinalis*. The juice of *asparagus*, in the state in which it comes to table, yields, as already stated (p. 1465,) a product, which has been termed *asparagine*; it also contains a little albumine, wax, and resin. The residue of the asparagus, which constitutes its eatable part, for boiling probably abstracts the matters contained in its expressed juice, has not been examined; nor have we any accurate information as to the cause of the singular odor which it imparts to the urine: it has been said, however, that *asparagine* is diuretic, and gives the urine the same odor.

*Aspidium filix mas*. (*Nephrodium*.) Male fern-root contains, according to Morin, a trace of volatile oil, fat oil, sugar, starch, tannine, pectine, malic and gallic acids combined with lime and potassa, phosphate of lime, and lignine; its ashes yielded silica, alumina, and oxide of iron. See also the abstract of a paper on fern-root by Dr. Luck. (*Chem. Gaz.*, Sept., 1845.) The anthelmintic property of this root, or rhizome, is said to reside in the volatile oil. An alkaloid (*filicina*) is also said to have been found in it.

*Athamanta oreoselinum*. Winkler describes a peculiar crystallizable principle in the root of this plant, soluble in alcohol, ether, and oils, but insoluble in water: its composition is  $C_{24}H_{15}O_7$ . (*Chem. Gaz.*, Jan. and Aug., 1843.) It has a peculiar rancid odor, and yields *valerianic acid* when subjected to dry distillation. (SCHNEIDERMAN and WINKLER, *Ann. der Pharm.*, li. 315.)

*Atropa belladonna*. (See *Atropia*, p. 1452.) 100lbs of the fresh herb yield about 2 lbs. 8 oz. of *pharmaceutical extract*. There are no good analyses of the parts of this plant.

*Avena sativa*. The common oat. Vogel gives the following as the composition of oats and oatmeal.



| The entire Seeds. |       | Dried Oatmeal.               |        |
|-------------------|-------|------------------------------|--------|
| Meal.....         | 66    | Starch .....                 | 59·00  |
| Husk .....        | 34    | Bitter matter and sugar .... | 8·25   |
|                   | <hr/> | Albuminous matter .....      | 4·30   |
|                   | 100   | Fatty oil .....              | 2·00   |
|                   |       | Gum.....                     | 2·50   |
|                   |       | Husk, moisture and loss....  | 23·95  |
|                   |       |                              | <hr/>  |
|                   |       |                              | 100·00 |

According to Christison, oatmeal consists of

|                                    |       |
|------------------------------------|-------|
| Starch .....                       | 72·8  |
| Saccharomucilaginous extract ..... | 5·8   |
| Albumine .....                     | 3·2   |
| Oleoresinous matter .....          | 0·3   |
| Lignine .....                      | 11·3  |
| Moisture .....                     | 6·6   |
|                                    | <hr/> |
|                                    | 100·0 |

The effect of different manures in modifying the composition of oats, is not, according to Hermstädt, very great. (See his table as given by Johnston, *Lectures on Agricultural Chemistry*, p. 745.)

*Bebearu* (or *Greenheart* of British Guiana) contains, according to MacLagan and Tilley, a bitter but not crystallizable basic substance, *Bebearine*, =  $C_{35}H_{20}O_6N$ .

*Berberis vulgaris*. The root yielded 2·55 of brown coloring matter precipitable by acetate of lead; 6·62 of a fine yellow extract (see *Berberine*, p. 1523) not so thrown down; gum 0·35, starch 0·2, oil 0·4, soft resin 0·55, lignine 55·4, water, earthy and alkaline salts, &c., 35. According to Fleitmann, *Berberine*, which by Buchner is represented as a weak acid, forms definite crystallizable compounds with the acids; he therefore regards it as an *organic base*, and represents it by the formula  $C_{42}H_{18}O_9N + 2HO$ . (*Ann. der Pharm.*, xlix. 160. Löwig, ii. 1697.) The barberry bark also contains, according to Pölex, a white pulverulent substance which he calls *oxyacanthine*. (Löwig, ii. 1716.)

*Beta vulgaris*. There are no good analyses of the varieties of *beet-root*. According to Hermstädt, as quoted by Schubler, the *sugar beet* contains about 5 *per cent.* of starch and gum, 10 of sugar, and 85 of water; but this can only be an approximate result. From a table given by Dr. Thomson, (*Veg. Chem.*, 813,) it appears that in 27 varieties of beet, the proportion of sugar varies from 5·8 to 10 *per cent.* (See also page 1178.)

*Bignonia chica*. The leaves afford a red coloring matter, used by the inhabitants of South America as a dye-stuff. The natives paint themselves with it.

*Boletus juglandis*, *laricis*, and *pseudo-igniarius*, have been examined by Braconnot. (*Ann. de Chim.*, lxxx. 273.)

*Brassica oleracea*. *Cabbage*. The fresh leaves yield, *per cent.* 0·63 green fecula, 0·29 albumine, 0·05 resin, 2·89 gum or mucilaginous extract, 2·84 extract soluble both in alcohol and water. The saline matters are sulphate and nitrate of potassa, chloride of potassium, malate and phosphate of lime, phosphate of magnesia, and oxides of iron and manganese. (Schrader.) So that, according to this analysis, the cabbage may be

assumed to contain about 7 *per cent.* of nutritive matter, the remainder being lignine and water.

*Brassica rapa.* Turnips contain about 7.5 *per cent.* of solid matter, and 92.5 water. (BOUSSINGAULT.)

*Bryonia alba.* According to Brandes and Firnhaber the root contains bryonine and a little sugar 1.9, resin and a little wax 3.4, mucilage, gum, starch, and pectine 29.4, albumine 6.5, extractive 1.7, lignine 15.25, water 20. Bryonine is a bitter, acrid, crystalline substance. (See DULONG, *Journ. de Pharm.*, xii. 158 and 507.)

*Buxus sempervirens.* The leaves of box contain a white, bitter, pulverulent principle, which is acrid and alkaline, soluble in water and alcohol, and very sparingly soluble in ether. Its compounds with the acids are not crystallizable. (FAVRE, *Journ. de Pharm.*, xvi. 428.)

*Calendula officinalis.* The *marigold* petals contain yellow-green soft resin 3.44, bitter extractive 19.13, gum 1.5, starch 1.25, mucilage (*Calenduline*, p. 1193,) 3.50, albumine 0.62, free malic acid with bitter extractive 6.84, malate of potassa 5.45, malate of lime 1.47, chloride of potassium 0.66, lignine 62.5. (This gives an excess = 7.33.) The leaves contain the same substances, and a little nitrate of potassa. (GEIGER, *Dissert. de Calendula.* Heidelberg, 1819.)

*Cannabis sativa.* Hempseed contains, according to Bueholz, 19.1 *per cent.* of oil: the residuary cake contains 24.7 *per cent.* of albumine, 43.3 of lignine and other insoluble matters; gum, sugar, and a trace of bitter extractive, constitute the residue.

*Capsicum annuum.* Bueholz found in the pods of *capsicum*, 7.6 wax, 4 acrid resin, 8.6 bitter aromatic extract, 21 gum and extractive, 9.2 gum, 3.2 albumine, 28 lignine, 12 water, loss 6.4. Braconnot terms the acrid soft resin, which appears to constitute the active principle of this pepper, *capsicine*; it fuses when heated, and a single grain, vaporized in an ordinary sized room, is so diffused through the air as to cause it to excite coughing and sneezing. (*Ann. Ch. et Ph.*, iv. 122.)

*Caryophyllus aromaticus.* *Eugenia caryophyllata.* Cloves are the calyces and buds of this plant. They contain, volatile oil 18.0, tannine 13, extractive 4.0, tasteless resin 6.0, gum 13, lignine 28, moisture 18. (TROMMSDORFF.) By repeated distillation, Ostermeyer obtained 21.5 essential oil; he also obtained the oil of cloves, by *expression*; it then contained a peculiar kind of wax. The average produce of essential oil, as obtained from repeated experiments at Apothecaries Hall, does not exceed 10 *per cent.* (See *Oil of Cloves*, p. 1544.)

*Cassia fistula.* The pulp of the seed-pods of an American, and also of an African variety of this tree, yielded, sugar 69.25, gum 2.6, tannine 3.9, water 24.25; ii., sugar 61.0, gum 6.75, tannine 13.25, water 19.0. (HENRY.) This pulp is medicinally used as a purgative. Caventou found a bitter principle (*Cassine*) in the root of the *Cassia fistula*. (*Journ. de Pharm.*, xiii. 340.)

*Cassia Senna.* The existence of a purgative bitter principle in these leaves (*cathartine*) has been announced by Lassaigne and Feneulle. (*Ann. Ch. et Ph.*, xvi. 18.) It is said to be identical with *cytisine*, obtained from *Cytisus alpinus*. (See also Dr. A. T. THOMSON'S *London Dispensatory*.) 100 lbs. of senna leaves yield 50 lbs of *pharmaceutical extract*.

*Cetraria Islandica.* *Lichen Islandicus.* Iceland moss has been



somewhat minutely examined by Berzelius; the details of the analysis are given in his *Lehrbuch*. The result is, green-wax 1·6, yellow coloring extractive 7·0, bitter principle 3·0, sugar 3·6, gum 3·7, starch 44·6, starchy lignine 36·2; a trace of gallic acid, tartar, tartrate of lime, and phosphate of lime 1·9. It has also been analyzed by John, with the following results: green resin 1·5, extractive 10, inuline 8·0, modified inuline 40·0, insoluble parts 37·5, saline substances 3·0. (See an elaborate series of experiments on this lichen by Schnedermann and Knop. *Annalen der Pharm.*, LV. *Chem. Gaz.*, Jan. and Feb., 1846.)

*Centaurea benedicta*. The dried herb yields volatile oil, chlorophylle and fat oil, brown resin, extractive bitter principle, sugar, gum, albumine, ligneous matter, and various salts. (MORIN, *Journal de Chim. Med.*, iii. 105.) According to Scribe (*Comptes Rendus*, xvi. 802), the leaves of *Centaurea benedicta*, *calcitrapa*, &c., and of the *cynareæ* generally, contain a crystallizable bitter substance, which he designates *Cnicine*, = C<sub>28</sub> H<sub>18</sub> O<sub>10</sub>. (See also NATIVELLE, *Erdmann and Marchand's Journ.*, xxxii. 93.)

*Cephaelis ipecacuanha*. Ipecacuanha root has been examined by Pelletier and Majendie, and an account of their researches is published by Robiquet, in the *Ann. Ch. et Ph.*, iv. 172. 100 parts of this root, deprived of the woody fibre which traverses its centre, afforded, fatty matter 2, emetina 14, gum 16, starch 18, woody fibre 48, a trace of wax, loss 2. The means of separating the *emetie principle* have already been described. (See p. 1463.)

*Chondrus crispus*. *Carageen*, *Irish*, or *Pearl Moss*, is used medicinally, and as an article of diet: it contains, according to Pereira,

|  |             |
|--|-------------|
| Vegetable jelly ( <i>carageenine</i> ) .....   | 79·1        |
| Mucilage .....   | 9·5         |
| Resin .....  | 0·7         |
| Fat, and free acid.....  | traces      |
| Salts, containing chlorine, iodine, bromine, sodium, magnesium, }<br>potassium, calcium..... | 10·7        |
|  | <hr/> 100·0 |

*Chamærops humilis*? The leaves of this palm are imported from Cuba, and other parts of the West Indies, into the United States of America, for the purpose of being made into hats. The leaf is covered by a natural varnish which is a true *vegetable wax*. It has been described and analyzed by Teschemacher. (*Mem. Chem. Soc.*, iii. 24.)

*Cichorium intibus*. The leaves of succory bruised and fermented, yield a blue coloring-matter. (The process for its preparation has been patented by Mr. Metcalfe, of Leeds, November, 1844.) The roasted root is much used in Germany and elsewhere, as a substitute for coffee: it has not been satisfactorily analyzed. According to Juch it contains a small quantity of bitter extractive and of resin and sugar, the residue being lignine. Enormous quantities of roasted succory are prepared in London, and used for the adulteration of ground coffee.

*Cinchona lancifolia*, *cordifolia*, and *oblongifolia*, and other species. (See *Cinchonia*, *Quinia*, &c.) The varieties of Peruvian bark have been examined by Pelletier and Caventou. In the *Cinchona lancifolia*, or *pale bark*, they found the following constituent parts: 1. cinchonia,

combined with kinic acid; 2. green fatty matter; 3. red and yellow coloring matter; 4. tannine; 5. kinate of lime; 6. gum; 7. starch; 8. lignine.

In *yellow bark* they found, 1. quinia, with kinic acid; 2. yellow fatty matter; 3. yellow coloring matter; 4. tannine; 5. kinate of lime; 6. starch; 7. lignine. In *red bark* the same substances as in the two former. There can be no doubt that the tannine, and probably the coloring extractives, as well as the alkaloids and the kinic acid, all contribute to the medical efficacy of these barks. The produce in *pharmaceutical extract*, of *pale bark*, is about 36 per cent. (See p. 1427, *et seq.*)

*Cissampelos Pareira*. The root of this plant, usually termed *Pareira brava*, and called by the Germans *Grieswurzel* (or *gravel-root*) from its beneficial effects in stone and gravel, has been analyzed by Feneulle, (*Journ. de Pharm.*, vii. 404,) and by Wiggers. (*Ann. der Pharm.*, xxiii. 81.) Its active principle appears to be a yellow bitter extract, not crystallizable, but having basic characters. It has been termed *Cissampeline* and also *Pelosine*.

*Citrus aurantium* and *medica*. Neither *oranges*, nor *lemons*, have been subjected to any accurate examination. Dried orange-peel yields from 16 to 20 per cent. of an agreeable and apparently peculiar bitter extract. Lemon juice contains, according to Proust, 97·51 water, 1·77 citric acid, with bitter extract, gum, and a trace of malic acid, amounting together to 0·72 per cent. A peculiar crystallizable nonazotic and bitter principle is stated by Schmidt to be contained in the seeds of lemons, oranges, and other *aurantiaceæ*. (*Chem. Gaz.*, Jan., 1845.) An elaborate analysis of the *ashes* of different parts of the orange-tree has been published by Rowney and How. (*Mem. Chem. Soc.*, iii. 370.) According to Lebreton (*Journ. de Pharm.*, xiv. 377), an insipid white crystalline substance may be extracted from the soft spongy part of orange and lemon-peel; it is inodorous, little soluble in water and cold alcohol, and insoluble in ether, but very soluble in boiling alcohol, and in alkalis and acetic acid. It is neither acid nor basic: when gently heated it fuses, and at a higher temperature is decomposed; but it is not volatile. It has been termed *Hesperidine*, and also *Aurantiine*. (See JONAS, *Archiv. für Pharm.*, xxvii. 186, and LÖWIG, *Chem. d. Org. verbind.*, i. 780.)

*Cocculus Palmatus*. This plant abounds in the forests of Mozambique, on the east side of Southern Africa: the sliced and dried root is known under the name of *Calumba*. It has been analyzed by Planche and by Buchner, and Wittstock discovered in it a crystallizable bitter principle (*Calumbine*), afterwards analyzed by Liebig, consisting, per cent. of C66·36, H6·17, O27·47. (*Poggend. Ann.*, xix. 298, and xxi. 30.) Calumbine is deposited on cooling the hot and concentrated alcoholic tincture of the root, and may be purified by animal charcoal. It is very little soluble at common temperatures either in water, alcohol, or ether. It is very soluble in the alkalis. When heated it fuses like wax. Calumba root abounds in a peculiar mucilaginous matter, which renders its aqueous infusion very liable to decomposition.

*Cochlearia armoracia*. *Horseradish*. Einhof obtained from 4 pounds of the fresh root, 3 lbs. 2 oz. water, 20 grs. volatile oil, 31·5 grs. albumine, 1·5 oz. and 20 grs. of starch, 1·5 oz. of gum and sugar, 6 grs. bitter resin,



1 drachm 41 grs. acetate of lime, sulphate of lime, and acetic acid, 8 oz. lignine. The volatile oil contains sulphur. (See p. 1567.)

*Cochlearia officinalis*. *Scurvy grass*. The extract of the expressed juice contains brown sweet extract, soluble in hot alcohol, and precipitable by chlorine and by tannine, 48·33: matter insoluble in alcohol, but precipitable by tannine, 32·00; salts of potassa with vegetable acids 15·3. The fresh plant contains a sulphurous acrid oil, and sometimes nitre.

*Coffea Arabica*. The leaves of the coffee plant are employed in Java and Sumatra as a substitute for tea, of which they have the odor and flavor, and probably contain *theine*. For the analysis of coffee seeds, see p. 1468.

*Colchicum autumnale*. (See *Colchicia*, p. 1452.) The bulbs contain a fatty matter resembling that of veratria, and of sabadilla seed? also gum, inuline, starch, extractive, gallic acid, colchicia, and lignine. 100 lbs. of the recent bulbs yield between 18 and 19 lbs. of *pharmaceutical extract*.

*Conium maculatum*. (See *Conia*, p. 1457.) 100 lbs. of fresh hemlock yield an average produce of 4 lbs. of *pharmaceutical extract*.

*Convolvulus jalapa*. *Ipomœa purga*. *Jalap root*, analyzed by Cadet de Gassicourt, (see p. 1578,) yielded 10 resin, 5 starch and albumine, 44 gummy extract, 28 lignine, exclusive of salts, water, and loss. The average produce of *pharmaceutical extract of jalap* (*London Pharm.*) is 66 *per cent*. An elaborate analysis of jalap root, by Kayser, is given in the *Ann. der Pharm.*, Li. 81.

*Cornus florida*. The bark of the root of this tree, which is a native of North America, and is used as a febrifuge, has been analyzed by Geiger: it contains *cornic acid*, much tannine, and a peculiar bitter crystallizable substance (*Ann. der Pharm.*, xiv. 206.)

*Crocus sativus*. From 100 parts of fine *saffron*, Bouillon Lagrange and Vogel obtained yellow volatile oil, with fat, 7·5; wax 0·5; *polychroite* 65; gum 6·5; albumine 0·5; lignine 10; water 10. Saffron, as it occurs in trade, is often very damp, and mixed with 5 or 6 *per cent*. of sand.

*Croton cascarilla*. *Croton Eleutheria*. Cascarilla bark, analyzed by Trommsdorff, gave 1·6 volatile oil, 15·5 bitter soft resin; 18·7 bitter gummy extractive; 65·6 lignine. (*Ann. de Chimie*, xxii. 219.) 100 lbs. of cascarilla bark yield about 30 of *pharmaceutical extract*.

*Cucumis colocynthis*. According to Meissner, the pith freed from seeds, contains fat oil 4·2; a yellow, brittle, very bitter resin, insoluble in ether, 13·2; *colocyntine* 14·4; gelatinous matter 3·0; gummy extractive 17·6; lignine 19: the remainder being water and salts. *Colocyntine* is not crystallizable, but may be separated in the form of an intensely bitter and cathartic extract, soluble in water, alcohol, and ether.

*Cucumis sativus*. *Cucumbers* have been examined by John, who found in the peeled cucumber, green coloring-matter 0·04; sugar, with extractive, 1·66; soluble albumine 0·13; fibres, softened by boiling, and containing traces of phosphate of lime, 0·53; mucilage, free phosphoric acid, salts of ammonia, potassa, lime, and iron, with malic, phosphoric, sulphuric, and hydrochloric acids, 0·5. Water 97·14. The peel of the cucumber contained the same substances, but only 85 *per cent*. of water, and the fibre resembled fungine.

*Cusparia febrifuga*. The bark of this tree, known under the name of *Angustura bark*, contains a crystallizable substance which has been described by Saladin, who terms it *Cusparine*. (*Journ. de Chim. Med.*, ix. 388.)

*Cyclamen Europæum*. The root contains an aerid crystalline principle (*arthanatine*) discovered by Saladin, and examined by Buchner and Herberger. (*Repertorium*, xxxvii. 36.) In pharmacy this root has been termed *radix arthanitæ*.

*Daphne mezereon*. Gmelin and Bär obtained from *mezereon bark*, *daphnine*, wax, aerid resin, yellow coloring-matter, a saccharine and brown extract, gum, malic acid, lignine and several salts. *Daphnine* is a crystallizable substance of a bitter astringent taste, neither acid nor basic. (VAUQUELIN, *Ann. de Chim.*, lxxxiv. 173. GMELIN, *Schweigger's Journ.*, xxxv. 1.)

*Datisca cannabina*. From this plant Braconnot obtained *Datiscine*, a substance imperfectly crystallizable, and having the appearance of grape-sugar. (*Trommsdorff's Journal*, ii. 130.)

*Datura stramonium*. The fresh leaves of the *thorn-apple* contain 0·64 green fecula; 0·15 albumine; 0·12 resin; 0·60 extractive; 0·58 gum; 0·23 difficultly-soluble salts; 5·15 lignine; 91·25 water. (PROMNITZ.) (See *Daturia*, p. 1455.) 100 lbs. of the fresh herb afford an average produce of 2 lbs. 12 oz. of the *pharmaceutical extract*.

*Daucus carota*. Carrots have been mentioned as a source of pectine, (p. 1194.) Hermbstädt obtained 6½ lbs. of syrup from 124 lbs of carrot. The common carrot afforded 10·75 of starch and pectine, 7·8 of saccharine matter, and 1·1 albumine, *per cent.*, the remainder being fibre and water. Wackenroder obtained a red crystalline substance, *Carotine*, and a little fatty matter. (*Mag. für Pharm.*, xxxiii. 148.)

*Delphinium staphisagria*. Brandes found in *stavesacre seeds*, stearine 1·4, oil 19·1, gum 3·15, starch 2·40, an azotized extractive, insoluble in alcohol, precipitable by acetate of lead and by infusion of galls, with traces of various salts, 30·65, *delphia* 8·10 (see p. 1455), albumine 4·12, sulphates and phosphates of potassa, lime, and magnesia, 5, water 10.

*Digitalis purpurea*. The leaves of the *foxglove* contain, according to Rein and Haase, a soft, viscid, green resin, soluble in ether, alcohol, and volatile oils 5·5, extractive 15·0, superoxalate of potassa 2·0, lignine 52·0, water 5·5 (loss 5.) The activity of digitalis resides, according to Haase, in the soft resin. (See *Digitalia*, p. 1460.)

*Ervum Lens*. Lentils contain, according to Einhof,

|                             |       |
|-----------------------------|-------|
| Husk .....                  | 18·7  |
| Legumine and albumine ..... | 38·5  |
| Starch .....                | 32·8  |
| Sugar .....                 | 3·1   |
| Gum .....                   | 6·0   |
| Fat .....                   | ?     |
| Salts and loss .....        | 0·9   |
|                             | <hr/> |
|                             | 1·000 |

*Escholtzia Californica*. The root of this plant, now common in our flower-gardens, abounds in a yellow bitter juice. According to Walz, three alkaloids, or basic substances are contained in it, namely, one in



the root, and two in the leaves and stem. (*Jahrbuch für prakt. Pharm.*, viii. 223. LÖWIG, ii. 1702.)

*Esenbeckia febrifuga* contains, according to Buchner (*Repert.*, xxxvii. 1,) an organic basis, (*Esenbeckia*.)

*Eupatorium cannabinum* is stated, upon the authority of Righini, to contain a bitter alkaloid (*Eupatoria*,) giving a crystallizable salt with sulphuric acid. (*Mag. für Pharm.*, xxv. 98.)

*Fragaria vesca*. *Strawberries* have never been analyzed. Dried in *vacuo*, over sulphuric acid, they lose about 90 per cent. According to Scheele, the acid which they contain consists of equal parts of malic and tartaric acids. Their fragrantcy passes over in distillation with water.

*Gentiana lutea*. According to Henry and Caventou, (*Ann. of Phil.*, xvi. 98,) gentian contains the following substances: 1. a substance resembling bird-lime; 2. a resin combined with oil, which gives to gentian its peculiar odor; 3. a bitter extractive principle; 4. gum and coloring matter; 5. phosphate of lime? 100 lbs. of gentian root yield about 62 of pharmaceutical extract. The *bitter principle* of gentian, called by Henry *gentianine*, is, according to Leconte, (*Journ. de Pharm.*, xxiii. 465,) an *acid*; but Trommsdorff ascribes the bitterness of gentian to a *resin*, and applies the term *gentianine* to a yellow crystalline and insipid substance almost insoluble in water, but more soluble in alcohol and ether. (*Ann. der Pharm.*, xxi. 134.)

*Geoffroya Surinamensis*. The bark contains a crystallizable principle, which forms crystalline salts with sulphuric and hydrochloric acid. It has been termed *Surinamine*. (HUTTENSCHMIDT, *Mag. für Pharm.*, vii. 287.) The same chemist finds a crystallizable substance in the bark of *Geoffroya Jamaicensis*, which he calls *Jamaicine*.

*Glycyrrhiza glabra*. Two of the components of *liquorice root* have already been mentioned, namely, a peculiar *sugar*, and *asparagine*, (pp. 1189 and 1465.) Robiquet found in it the following substances (*Ann. de Ch.*, LXX.): 1. starch; 2. gluten; 3. liquorice sugar; 4. phosphate and malate of lime and magnesia; 5. an acrid oil; 6. a crystallizable substance (*asparagine*); 7. woody fibre.

*Gracilaria lichenoides*. *Ceylon or Jafna Moss*, a whitish, filamentous sea-weed brought from India: it contains, according to Pereira,

|                      |       |
|----------------------|-------|
| Vegetable jelly..... | 54·5  |
| Starch .....         | 15·0  |
| Lignine.....         | 18·0  |
| Gum .....            | 4·    |
| Salts, &c. ....      | 8·5   |
|                      | <hr/> |
|                      | 100·0 |

*Gratiola officinalis*. The purgative properties of this plant are referred by E. Marchand to a crystallizable principle, which he terms *gratioline*. (*Journ. de Med.*, 1845.)

*Guaiacum officinale*. *Lignum vitæ*. Hagen obtained 3 per cent. of *resin of guaiacum* (p. 1577) from this wood. From 1 ounce of rasped wood Trommsdorff obtained (in different samples) from 35 to 160 grains of matter soluble in alcohol, and from 45 to 96 grains of watery extract. When guaiacum wood is boiled in water, a small portion of

soluble matter is dissolved; the residue becomes blue by exposure to air. (*Phil. Trans.*, 1811.)

*Helvella mitra.* Morels contain, according to Schrader, stearine and elaine 4·0, sugar 2·0, azotized extractive (*vegetable osmazome*) 29·4, gummy azotized extractive 5·4, albumine 1·2, boletate and phosphate of ammonia and potassa 8·0, fungine 39·6, water 10·4. It is evident that the peculiar flavor and characters of mushrooms, and similar articles of food, are referable to the extractive matter containing nitrogen, and hence resembling an animal product, which I have above termed *vegetable osmazome*: this substance deserves further examination, especially by the culinary chemist.

*Hippophae rhamnoides.* The berries contain a peculiar coloring-matter. (*Chem. Gaz.*, March, 1844.)

*Hordeum distichon*, &c. The following, according to Einhof, is the composition of barley:—

| The Ripe Seeds. |              | Barley Meal.   |              |
|-----------------|--------------|--|--------------|
| Meal...         | 70·05        | Starch.....  | 67·18        |
| Husk .....      | 18·75        | Fibrous matter {<br>glutine<br>starch<br>lignine } ... | 7·29         |
| Moisture .....  | 11·20        | Gum .....  | 4·62         |
|                 | <hr/> 100·00 | Sugar .....  | 5·21         |
|                 |              | Glutine .....  | 3·52         |
|                 |              | Albumine .....   | 1·15         |
|                 |              | Phosphate of lime .....                                | 0·24         |
|                 |              | Moisture .....   | 9·37         |
|                 |              | Loss.....  | 1·42         |
|                 |              |  | <hr/> 100·00 |

*Humulus lupulus.* Hops yield about 27 per cent. of *pharmaceutical extract*. The pure bitter extractive of the hop has been called *Lupuline*, but that term was first applied by Dr. Ives, of New York, to the pollen, or, as it is technically called, the *condition* of the hop, and which consists of 36 resin, 12 wax, 11 bitter extract (*lupuline*), 5 tannine, 10 extractive insoluble in alcohol, and 46 insoluble residue. (See PAYEN and CHEVALLIER, *Journ. de Pharm.*, viii. 216.) According to H. Watts, (*Mem. Chem. Soc.*, iii. 392,) hops, in their usual marketable state, lose between 11 and 12 per cent. by drying at 212°, and leave when burned, between 6 and 7 per cent. of ash, consisting of

|                             |              |                                   |
|-----------------------------|--------------|-----------------------------------|
| Chloride of sodium .....    | 1·32         | } 35·58 matters soluble in water. |
| Chloride of potassium ..... | 3·09         |                                   |
| Carbonate of potassa .....  | 6·79         |                                   |
| Sulphate of potassa.....    | 18·05        |                                   |
| Phosphate of potassa .....  | 2·50         |                                   |
| Silicate of potassa .....   | 3·83         | } 46·03 matters soluble in acids. |
| Carbonate of lime .....     | 11·04        |                                   |
| Carbonate of magnesia ..... | 7·73         |                                   |
| Phosphate of lime .....     | 14·64        |                                   |
| Phosphate of magnesia ..... | 4·37         |                                   |
| Phosphate of alumina .....  | 3·68         |                                   |
| Phosphate of iron .....     | 4·57         | } 18·39 insoluble matter.         |
| Silica, &c.....             | 15·44        |                                   |
| Charcoal and loss.....      | 2·95         |                                   |
|                             | <hr/> 100·00 |                                   |



*Hyoscyamus niger*. *Henbane* requires to be minutely examined. (See *Hyoscyamia*, p. 1453.) 100 lbs. of the herb yield, upon an average,  $3\frac{1}{4}$  lbs. of *pharmaceutical extract*. *Henbane seed* contains, according to Brandes, 24·2 oil, 1·4 stearine, a trace of sugar, 1·2 gum, 2·4 mucilage, 1·5 starch, 3·4 extractive, 4·5 albumine, 26· lignine, 24· water: various salts, and a trace of *copper*? They have since been found to contain *hyoscyamia*.

*Ilex aquifolium*. The leaves of this plant yield a bitter crystalline principle called by Déleschamps *Ilicine*. (*Buchner's Repert.*, xxxix.)

*Ilex Paraguayensis*. *Paraguay tea*. The leaves are used in South America as a substitute for tea, and, according to Stenhouse, contain *theine*. (See p. 1467.)

*Inula helenium*. (See *Inuline*, p. 1168.) Elecampane root contains, volatile oil 0·4, wax 0·6, acrid soft resin 1·7, bitter extractive soluble in alcohol and water 36·7, gum 4·5, inuline 36·7, albuminous matter 13·9, lignine 5·5. (JOHN.) By the action of alcohol on the dried root a crystallizable substance is separated, which has been termed *Helenine*, (p. 1563) described and analyzed by Gerhardt. (*Ann. Ch. et Ph.*, Lxxii. 163.)

*Juglans regia*. The outer green husk of the unripe *walnut* contains resinous green matter, tannine, extractive, starch, citric and malic acid, oxalate and phosphate of lime, lignine; and, in the ash, potassa, and oxide of iron. The expressed juice is at first colorless, but becomes brown by exposure: it forms a good dye-stuff.

*Juniperus communis*. *Juniper berries* contain a volatile oil and sugar; the former is most abundant in the berries just at their period of ripening; when they are quite ripe and black, it has chiefly passed into resin. The sugar is most plentiful in the deep blue berries, and is partly decomposed when they blacken and dry. Trommsdorff found in the ripe berries, volatile oil (specific gravity 0·853) 1·0, brittle wax, soluble in hot alcohol, ether, and caustic potassa, 4·0, tasteless and inodorous resin 10 0, a peculiar kind of sugar 33·8, gum 7·0, lignine 35·0. The produce of essential oil, from the *German* berries, as ascertained by repeated distillations at Apothecaries' Hall, amounts upon an average to from 9 to 10 ounces from the 100 lbs., and from the *Italian* berries to 7 ounces. (See also NICOLET, *Journ. de Pharm.*, xvii. 310.)

*Krameria triandra*. This plant is a native of Peru; its root is known under the name of *Ratanhy*; it is of deep brownish-red color, and contains a large quantity of *tannine*, and, according to Peschier, a peculiar acid, which he calls *Krameric acid*. (*Journ. de Pharm.*, vi. 34.)

*Lactuca sativa*. The common lettuce, the inspissated juice of which is termed *Lactucarium* or *Thridacine*. It is a mild narcotic, and has been supposed to contain *morphia*; that principle, however, has never been detected in it. (CAVENTOU, *Journ. de Chimie Medicale*, i. 300.) A substance called *Lactucarium* has also been obtained from the *Lactuca virosa*, together with a peculiar acid (*Lactucic acid*), but which, according to Köhnke, is succinic acid. (*Chem. Gaz.*, Feb., 1845.) The *lactucarium* of the wild or strong-scented lettuce has been examined by Lenoir (*Chem. Gaz.*, Feb., 1847,) and by Walz, (*Ann. der Pharm.*,

xxxii. 85,) who obtained from it a bitter crystalline principle, *Lactucine*. (See also LUDWIG, *Chem. Gaz.*, November, 1847, p. 426.)

*Laminaria saccharina*. Stenhouse has found *mannite* in this and some other sea-weeds. (*Mem. Chem. Soc.*, ii, 136.)

*Laurus cassia*. The bark contains volatile oil 0·8, tasteless pale brown soft resin 4, gummy extract 14·6, lignine 64·3, water and loss 16·3. (BUCHOLZ.)

*Laurus cinnamomum*. The finest Ceylon cinnamon bark yields essential oil, a soft aromatic resin soluble in ether, tannine, extractive, gum, and above 80 per cent. of lignine. (VAUQUELIN. See p. 1389.)

*Laurus nobilis*. Bay berries have been examined by Bonastre: he found volatile oil 0·8, a crystallizable substance, which he calls *laurine*, 0·5, fat oil 9·9, soft resin 0·8, starch 12·95, gum 8·6, mucilage 3·2, sugar 0·2, lignine 9·4, water 3·2. They also contain a free acid. (*Journ. de Pharm.*, x. 32.)

*Leontodon taraxacum*. Dandelion root is stated by John to contain in its milky juice a portion of caoutchouc, besides sugar and gum, and a very small quantity of bitter extractive. 100 lbs of the fresh root yield about 11 lbs of *pharmaceutical extract*. Squires' experiments upon this root show that its expressed juice contains gum, albumine, glutine, an odorous principle, extractive, and *Taraxacine*, a crystallizable bitter principle. (BRANDE'S *Dictionary of Pharmacy*, 532.)

*Linaria vulgaris*. The flowers are used as a yellow dye. (RIEDEL, *Chem. Gaz.*, Aug., 1843.)

*Linum catharticum*. A bitter inodorous pulverulent substance, termed by Pagenstecher *Linine*, has been obtained from this plant: it appears to have weak basic properties. (*Buchner's Repert.*, xxvi. 313.)

*Liriodendron tulipifera*. An acrid bitter principle has been obtained by Emmet from the bark of the root of this tree. (*Journ. de Pharm.*, xvii. 400.) It crystallizes in acicular prisms, little soluble in water, but very soluble in alcohol and ether; it has been termed *Liriodendrine*.

*Lobelia inflata*, according to Pereira and Reinsch, contains a peculiar acrid oil, *Lobeline*? and an acid, *Lobelic acid*. (PEREIRA, *Mat. Med.* REINSCH, *Ch. Gaz.*, Aug., 1843.)

*Lupinus albus*. The seeds contain a bitter principle, which Cassola has termed *lupinine*. (*Journ. Chim. Med.*, x. 688.)

*Marantha arundinacea*. The root of this plant has been mentioned as a source of the species of starch, which we call *arrow-root*. The fresh root contains, according to Benzon, volatile oil 0·7, starch 26, albumine 1·58, gummy extract 0·6, lignine 6, water 65·6.

*Matico*. The leaves of a Peruvian plant said to be a species of pepper, have been brought under this name to England. It has been chemically examined by Dr. Hodges, who obtained from it a heavy volatile oil. (*Mem. Chem. Soc.*, ii. 123.)

*Melampyrum nemorosum*. Hünefeld obtained a crystalline substance (*Melampyrine*) from this plant: it is very soluble in water, and almost insipid.

*Melilotus officinalis*. The flowers contain *Coumarine*. (DELALANDE, *An. Ch. et Ph.*, 3ème Sér., Novemb., 1842. See also p. 1565.)

*Melissa officinalis*. Balm yields, according to Dehne, 1-1920th its  
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weight of volatile oil. The infusion of balm (often drunk as *balm tea*), contains tannine, extractive, and gum. Alcohol extracts a little resin.

*Menyanthes trifoliata*. From 100 parts of the fresh leaves, Trommsdorff obtained 15·6 lignine: the green expressed juice deposits, on boiling, 0·49 fecula, from which alcohol and ether abstract 0·12 soft green resin, and 0·37 albumine remains. The filtered juice yields 3·92 of extract, containing gum, inuline, and extractive; the extractive includes a peculiar bitter principle, *menyanthine*, and an azotized substance. (See *Brandes's Archiv. für Pharm.*, xxx. 153.)

*Momordica elaterium*. (*Squirting Cucumber*.) The substance known in pharmacy under the name of *Elaterium*, is the deposit of the strained juice of these cucumbers, as they are termed. When properly prepared, and carefully dried, it is of a pale greenish-grey color, and of an acrid bitterish taste: it is friable, and inodorous, and intensely purgative in doses considerably below one grain. *Elaterium* has been repeatedly analyzed, and appears, from the experiments of Paris, (*Pharmacologia*,) and of Hennell, (*Journ. Royal Instit.*, i. 532,) to contain a distinct active principle called *Elatine* or *Elaterine*. It is crystalline, and said to be insoluble in water, difficultly soluble in ether, but soluble in 5 parts of cold and 2 of boiling alcohol. It consists, according to Zwenger, of  $C_{20}H_{14}O_5$ , but there is much discrepancy in the results of the different analyses which have been made of it.

*Monarda punctata*. *Horsemint*. The essential oil of this plant is described by Arppe. (*Liebig's Ann.*, lviii. 41. *Chem. Gaz.*, December, 1846.)

*Mangifera Indica*. *Mango*. This fruit has been analyzed by M. Arequin. (*Ann. Ch. et Ph.*, xlvii. 20.) The seeds contain some tannine and much gallic acid.

*Myristica moschata*. *Nutmegs* contain, according to Bonastre, (*Journ. de Pharm.*, ix. 281,) fat oil (p. 1262) 31·6, volatile oil 6·0, starch 2·4, gum 1·2, free acid 0·8, lignine 54, (loss 4.) The usual produce in *volatile oil*, in the distillations at Apothecaries' Hall, is 4·5 per cent.

*Myrtus pimenta*. *Allspice* has been examined by Bonastre, (*Journ. de Pharm.*, xi. 180): he analyzed the outer shell and the kernel, with the following results:—

|                               | Husks. |       | Kernels. |
|-------------------------------|--------|-------|----------|
| Volatile oil.....             | 10·0   | ..... | 5·0      |
| Green soft resin.....         | 8·0    | ..... | 2·5      |
| Concrete fixed oil .....      | 0·9    | ..... | 3·2      |
| Tannine and extractive.....   | 11·4   | ..... | 39·8     |
| Gum .....                     | 3·0    | ..... | 7·2      |
| Brown gelatinous matter ..... | 4·0    | ..... | 3·8      |
| Resinous substance .....      | 1·2    | ..... | 1·2      |
| Saccharine extract.....       | 3·0    | ..... | 8·0      |
| Malic and gallic acids .....  | 0·6    | ..... | 1·6      |
| Lignine .....                 | 50·0   | ..... | 16·0     |
| Saline ash .....              | 2·8    | ..... | 1·9      |
| Moisture .....                | 3·5    | ..... | 3·0      |
| Loss.....                     | 2·2    | ..... | 8·8      |

*Nicotiana Tabacum.* The following are the results of a series of experiments made in 1845 by Mr. Cooper and myself, for the purpose of ascertaining the quantity of soluble and insoluble matter in eight samples of tobacco, of detecting the presence and quantity of sugar contained in them, and the nature and relative proportions of their inorganic constituents. An important paper on the state in which *nicotina* exists in tobacco, and on the relative proportion of it afforded by different varieties of the plant, has been published by Schloessing. (*Ann. Ch. et Ph.*, 3ème Sér., xix. 230.)

| Tobaccos,<br>dried at 212°.                  | Per cent. of Extract,<br>&c. soluble in water. | Per cent. of Woody<br>Fibre, &c. insoluble<br>in water. | Per cent. of Ash after<br>treating with Carbo-<br>nate of Ammonia. | Per cent. of matter<br>soluble in water in<br>the ash. | Per cent. of matter so-<br>luble in Hydrochlo-<br>ric Acid in the ash. | Per cent. of insoluble<br>matter, as Silica, &c.,<br>in the ash. | Per cent. of Alcohol<br>obtained from fer-<br>mented infusion. | Per cent. of Saccharine<br>matter, deduced from<br>the obtained Alcohol. |
|--|--|---|--|--|--|--|--|--|
| 1. Light Missouri, }<br>leaf and stalk.... } | 49·  | 54·9  | 20·97<br>white   | 2·17   | 11·73  | 5·9  |  |  |
| 2. Light Missouri, }<br>leaf only..... }     | 50·  | 47·7  | 19·7<br>white  | 1·77   | 12·83  | 5·1  | 0·75   | 1·50   |
| 3. Dark Missouri, }<br>leaf and stalk.... }  | 50·  | 52·4  | 16·47<br>white   | 4·2  | 10·14  | 2·13   |  |  |
| 4. Dark Missouri, }<br>leaf only..... }      | 51·  | 50·6  | 13·8<br>white  | 2·17   | 8·73   | 2·9  | 0·35   | 0·71   |
| 5. Light Virginia, }<br>leaf and stalk.... } | 51·5   | 53·1  | 16·4<br>grey-<br>white   | 2·53   | 8·54   | 5·33   |  |  |
| 6. Light Virginia, }<br>leaf only..... }     | 54·  | 46·1  | 11·97<br>green-<br>grey  | 2·0  | 6·86   | 3·11   | 1·045  | 2·09   |
| 7. Dark Virginia, }<br>leaf and stalk.... }  | 48·5   | 51·8  | 14·7<br>grey   | 4·8  | 8·40   | 1·5  |  |  |
| 8. Dark Virginia, }<br>leaf only..... }      | 52·  | 49·8  | 12·53<br>grey  | 2·63   | 8·20   | 1·7  | 1·46   | 2·93   |

1. The samples were dried, and the extract and woody fibre were also dried at 212°. The watery infusions of all contained ammoniacal salts. The salts from the ash which were soluble in water, consisted of sulphates, carbonates, phosphates, and chlorides; the bases being potassa and lime. The solution by hydrochloric acid contained lime, alumina, phosphate of lime, and oxide of iron.
3. Contained oxide of manganese in small quantity. Sulphates in watery solution of ash, abundant. Hydrochloric solution contained an abundance of lime.
4. A trace of manganese; a trace only of phosphoric acid in watery solution.
5. Contained abundance of oxide of manganese.
6. Abundance of oxide of manganese.
7. A mere trace of oxide of manganese, and a trace of oxide of iron; only a trace of alumina.
8. A trace of oxide of manganese; quantity of oxide of iron very great; only a trace of alumina.



The following are the results of the analysis of the fresh leaves of tobacco, by Posselt and Reinmann. (*Mag. Pharm.*, xxiv. and xxv.)

|                                     |       |
|-------------------------------------|-------|
| Nicotina .....                      | 0·06  |
| Nicotianine .....                   | 0·01  |
| Bitter extract .....                | 2·87  |
| Gum.....                            | 1·74  |
| Resin .....                         | 0·27  |
| Glutine and albumine .....          | 1·31  |
| Malic acid .....                    | 0·51  |
| Malate of ammonia.....              | 0·12  |
| Sulphate of potassa.....            | 0·05  |
| Chloride of potassium .....         | 0·06  |
| Malate and nitrate of potassa ..... | 0·10  |
| Phosphate of lime .....             | 0·17  |
| Malate of lime.....                 | 0·24  |
| Silica .....                        | 0·09  |
| Lignine and a trace of starch.....  | 4·97  |
| Water .....                         | 88·28 |
| <hr/>                               |       |
| 100·85                              |       |

An elaborate analysis of the *ashes of tobacco* has been published by Will and Fresenius. (*Mem. Chem. Soc.*, ii. 192.)

*Ononis spinosa*. The root of this plant contains a slightly sweet crystalline principle, called by Reinsch *ononine*. (*Buchner's Repertor.*, xxviii. 18.)

*Orchis mascula*. The root, called *salep*, contains *starch* and *mucilage*.

*Oryza sativa*. The grain of *rice* has been analyzed by Braconnot, with the following results :

|                  | Carolina. |       | Piedmont. |
|------------------|-----------|-------|-----------|
| Water .....      | 5·0       | ..... | 7·0       |
| Husk .....       | 4·8       | ..... | 4·8       |
| Glutine .....    | 3·6       | ..... | 3·6       |
| Starch .....     | 85·07     | ..... | 83·8      |
| Sugar .....      | 0·3       | ..... | 0·05      |
| Gum .....        | 0·7       | ..... | 0·1       |
| Oil .....        | 0·13      | ..... | 0·25      |
| Phosphates ..... | 0·4       | ..... | 0·4       |
| <hr/>            |           | <hr/> |           |
| 100·0            |           | 100·0 |           |

Five varieties of rice, as sold in the shops, lost of *water* and gave of *ash*, per cent., as follows. (JOHNSTON.)

|                      | Water. |       | Ash. |
|----------------------|--------|-------|------|
| Madras rice.....     | 13·5   | ..... | 0·58 |
| Bengal rice .....    | 13·1   | ..... | 0·45 |
| Patna rice .....     | 13·1   | ..... | 0·36 |
| Carolina rice .....  | 13·0   | ..... | 0·33 |
| Carolina flour ..... | 14·6   | ..... | 0·35 |

By exposure to air the rice in a few days reabsorbed nearly all it had lost by drying. The ash of rice contains more alkali than that of wheat, and is very difficult of incineration.

*Paris quadrifolia*. A white crystalline substance of an acrid taste, has been extracted from this plant by Walz, (*Jahrbuch für prakt. Pharm.*, vi. 10) : he terms it *Paridine*, and represents it as C<sub>12</sub> H<sub>10</sub> O<sub>6</sub> + HO.

*Pastinaca sativa*. From 124 lbs. of parsneps Hermbstädt obtained  $5\frac{1}{2}$  lbs. of syrup: according to Drapier they yield (when dried?) 12 per cent. of sugar.

*Peganum Harmala*. The seeds of this plant, which grows in the steppes of Russia, contain a crystallizable alkaloid termed *Harmaline*. It was discovered by Göbel. (*Ann. der Pharm.*, xxxviii. 363, and *Revue Scientif.*, vii. 370.) It has been analyzed by Varrentrapp and Will, who represent it as  $C_{24}H_{13}O N_2$ . (*Ann. der Pharm.*, xxxix. 289. See also FRITZSCHE, *Berzelius' Jahrsbericht*, xxv. 530.)

*Peucedanum officinale*. *Sea sulphur wort*. Schlatter extracted from the root of this plant a crystallizable principle, which he calls *Peucedanine*. (*Ann. der Pharm.* v. 201.)

*Phaseolus vulgaris*. This is the common dwarf *kidney bean*, or *French bean*: the *Haricot* of the French. It is a distinct species from our *scarlet bean*, (*Phaseolus multiflorus*), the seed of which is not eaten. According to Einhof, as quoted by Johnston, (*Agricult. Chem.*, 755), the components of the kidney bean are

|                             |       |
|-----------------------------|-------|
| Water .....                 | 23·0  |
| Husk .....                  | 7·0   |
| Legumine, albumine, &c..... | 23·6  |
| Starch .....                | 43·0  |
| Sugar .....                 | 0·2   |
| Gum, &c. ....               | 1·5   |
| Oil and fat.....            | 0·7   |
| Salts and loss .....        | 1·0   |
|                             | <hr/> |
|                             | 100·0 |

*Phœnix Dactilifera*. *The date palm*. Dates have been analyzed by Reinsch, with the following results:—

| FLESH.                           |       | KERNEL.               |       |
|----------------------------------|-------|-----------------------|-------|
| Sugar.....                       | 58·0  | Fibre.....            | 39·6  |
| Pectine, gum, and bassorine .... | 15·4  | Gum, &c. ....         | 38·9  |
| Oil     }                        | 0·3   | Albumine .....        | 0·6   |
| Wax    }                         |       | Astringent acid ..... | 7·1   |
| Fibre .....                      | 2·3   | Fat .....             | 0·8   |
| Water .....                      | 24·0  | Water .....           | 13·0  |
|                                  | <hr/> |                       | <hr/> |
|                                  | 100·0 |                       | 100·0 |

*Phyllirea latifolia*, contains, according to Carbonici (*Pharm. Central Blatt*, 1837, p. 291,) a bitter crystalline principle, *phylliréine*, and also a peculiar acid.

*Phytolophas macrocarpa*. The seeds of this tree, known as *vegetable ivory*, have been examined by Connell, (*Phil. Mag.*, xxiv. 104,) and by Baumhauer, (*Chem. Gaz.*, March, 1845.)

*Pinus abies*. The well known aromatic odor of a forest of firs is ascribed by Gottschalk to an oil distinct from turpentine, obtained by distilling the fresh and young branches with water: its odor is intermediate between that of oil of lemon and orange; when rectified, its sp. gr. was ·856; its boiling point  $333^{\circ}$  F. It is isomeric with oil of turpentine, containing 88·3 carbon, 11·7 hydrogen. (WÖHLER, *Liebig's Ann.*, Aug. 1843.)

*Piper cubeba*. Soubeiran and Capitaine have described a peculiar



crystallizable substance obtained from cubebs, (*Cubebine*) ; it is inodorous and tasteless. Löwig could not succeed in obtaining it. (*Chem. der Org. verbind.*, i. 805.) Cubebs have also been analyzed by Monheim, (*Journ. de Pharm.* xx. 403,) according to whom they yield about 3·5 per cent. of volatile oil, and a principle termed *cubebine*.

*Pisum sativum*. The following, according to Braconnot, are the components of peas.

|                      |       |
|----------------------|-------|
| Water .....          | 12·5  |
| Husk .....           | 8·3   |
| Legumine ....        | 26·4  |
| Starch .....         | 43·6  |
| Sugar.....           | 2·0   |
| Gum .....            | 4·0   |
| Oil .....            | 1·2   |
| Salts and loss ..... | 2·0   |
|                      | <hr/> |
|                      | 100·0 |

*Polygala senega*. Senega root yields 7·5 soft resin, 6·15 *senegine*, 26·85 extractive, 9·5 gum and albumine, 46 lignine. (GEHLEN.) According to Quevenne (*Journ. de Pharm.*, xxii. 449,) the substance called by Gehlen *senegine*, is *polygalic acid*, the properties of which he has detailed at great length. (See also THOMSON'S *Veg. Chem.*, p. 162.)

*Polytrichum formosum*. (REINSCH, *Chem. Gaz.*, Sept. 1845.)

*Populus tremula*. The bark of this and other species of *populus* contains salicine, together with *populine*, a distinct principle, of a sweetish-bitter taste. (BRACONNOT, *Ann. Ch. et Ph.*, xliv. 296.)

*Prunus cerasus*. *Prunus Claudiana*. *Cherries*. *Green Gages*. These fruits have been analyzed by Berard, in different states of ripeness : he also examined *peaches*, *pears*, and *apricots* : the results are shown in the following table. (*Ann. Ch. et Ph.*, xvi. 152 and 225. *Sur la maturation des Fruits*.)

|                           | CHERRIES. |       | PLUMS. |        | PEACHES. |       | PEARS. |       | APRICOTS. |        |       |
|---------------------------|-----------|-------|--------|--------|----------|-------|--------|-------|-----------|--------|-------|
|                           | Green.    | Ripe. | Green. | Ripe.  | Green.   | Ripe. | Green. | Ripe. | Green.    | Riper. | Ripe. |
| Vegetable }<br>albumine } | 0 21      | 0·57  | 0·45   | 0·28   | 0·41     | 0·93  | 0·08   | 0·21  | 0·76      | 0·34   | 0·17  |
| Coloring }<br>matter.. }  | 0·05      | ..    | 0·03   | 0·08   | 0·27     | ..    | 0·08   | 0·01  | 0·04      | 0·03   | 0·10  |
| Lignine ..                | 2·44      | 1·12  | 1·26   | 1·11   | 3·01     | 1·21  | 3·80   | 2·19  | 3·61      | 2·53   | 1·86  |
| Gum ....                  | 6·01      | 3·23  | 5·53   | 2·06   | 4·22     | 4 85  | 3·17   | 2·07  | 4·10      | 4·47   | 5·12  |
| Sugar ....                | 1·12      | 18·12 | 17·71  | 24·81  | 0·63     | 11·61 | 6·45   | 11·52 | Trace     | 6·64   | 16·48 |
| Malic acid                | 1·75      | 2·01  | 0·45   | 0·56   | 1·07     | 1·10  | 0·11   | 0·08  | 2·70      | 2·30   | 1·80  |
| Lime ....                 | 0·14      | 0·10  | Traces | Traces | 0·08     | 0·06  | 0·03   | 0·04  | Trace     | Trace  | Trace |
| Water....                 | 88·28     | 74·85 | 74·57  | 71·10  | 90·31    | 80·24 | 86·28  | 83·88 | 89·39     | 84·34  | 74·87 |

*Punica granatum*. The rind of the *pomegranate* is used medicinally as an astringent : it contains, tannine 27·8, resin 0·9, extractive 32·8, gum 34·2, loss 5·1. (REUSS.) No lignine is here mentioned, so that the above are probably the soluble constituents only.

*Pyrus communis* and *malus*. *Pears* and *apples* have been examined by Berard, but there are many interesting points respecting them which

remain unnoticed, such especially as the rapid change which some of them undergo by the action of oxygen, when they are cut and exposed to air, and during which sugar appears to be formed; he also does not notice pectine or pectic acid, though perhaps it may be formed, as in *apple jelly*, by the action of heat upon their finely-divided lignine; he also overlooks tannine or gallic acid contained in many of those fruits, rendered evident by the blackening of the knives with which they are peeled. The following are the results which he obtained from *Beurré pears*, examined in three states, namely, i. ripe and fresh; ii. kept till mellow; iii. kept till brown or beginning to rot, and having lost 23·15 *per cent.* of water, &c.

|                                     | I.    |       | II.   |       | III.  |
|-------------------------------------|-------|-------|-------|-------|-------|
| Resinous green coloring matter..... | 0·08  | ..... | 0·01  | ..... | 0·04  |
| Sugar .....                         | 6·45  | ..... | 11·52 | ..... | 8·77  |
| Gum .....                           | 3·17  | ..... | 2·07  | ..... | 2·62  |
| Lignine .....                       | 3·80  | ..... | 2·19  | ..... | 1·85  |
| Albumine .....                      | 0·08  | ..... | 0·21  | ..... | 0·23  |
| Malic acid .....                    | 0·11  | ..... | 0·08  | ..... | 0·61  |
| Lime .....                          | 0·03  | ..... | 0·04  | ..... | trace |
| Water .....                         | 86·28 | ..... | 83·88 | ..... | 62·72 |

Apples contain the same ingredients as pears, but in somewhat different proportions, but the cause of the *flavor* and *aroma* of these fruits probably depends upon some volatile principle, which analysis has not detected.

*Pyrus cydonea*. According to Wöhler the odor of *quinces* is derived from an oil having the properties of *ænanthic ether*. (*Ann. der Pharm.*, xli. 240.)

*Quassia excelsa*. The wood of this tree, which has long been used in medicine as a powerful bitter, has not been minutely examined; it is said to contain a slight trace of volatile oil, a peculiar bitter extractive (*quassine*), gum, lignine, and salts. The bitter extractive is much more soluble in common alcohol than in water: it is precipitated, according to Pfaff, by acetate of lead: its aqueous solution, sweetened, is a good *fly-poison*.

*Quassia simarouba*. The bark, used in medicine, contains a volatile oil, bitter extract, traces of gallic acid, and many salts.

*Quercus robur*. *Oak bark*. 100 lbs. of oak bark yield, on an average, 20 lbs. of aqueous extract. According to Gerber, a crystalline principle, *Quercine*, may be extracted from oak bark. (*Archiv. für Pharm.*, xxxiv. 167.)

*Quercus suber*. An analysis of *cork*, by Döpping, is given in Liebig's *Annalen* for March, 1843, and in the *Chemical Gazette* for July, 1843. The bark of the cork-tree is sometimes called *Alcornoque bark*, but the American *alcornoque bark*, which contains a crystalline principle termed *Alcornine*, is derived from some other tree. (PEREIRA, *Pharm. Journ.*, vi. 362.)

*Rheum palmatum*. (See p. 1521, in reference to the *coloring matter* of rhubarb.) 100 lbs. of Indian rhubarb yield about 70 lbs. of aqueous extract.

*Rhus toxicodendron*. The juice of the leaves of this species, and of the *Rhus radicans* and *vernix*, contains an acrid poison, the nature of which has not been accurately ascertained: it is also a substantive *black dye*, extremely permanent; cotton or linen imbued with it acquiring a



deep black color by exposure: the nature of this coloring principle has not been examined, but it seems somewhat analogous to indigo.

*Ribes grossularia*. Gooseberries have been analyzed by Berard, with the following results.

|                                      | Unripe.     | Ripe. |
|--------------------------------------|-------------|-------|
| Resinous green coloring matter ..... | 0·03 .....  | —     |
| Sugar .....                          | 0·52 .....  | 6·24  |
| Gum .....                            | 1·36 .....  | 0·78  |
| Albumine .....                       | 1·07 .....  | 0·86  |
| Malic acid .....                     | 1·80 .....  | 2·41  |
| Citric acid .....                    | 0·12 .....  | 0·31  |
| Lime .....                           | 0·24 .....  | 0·29  |
| Lignine, including the seeds.....    | 8·45 .....  | 8·01  |
| Water.....                           | 86·41 ..... | 81·10 |

*Ricinus communis*. This seed, which affords *castor oil* (p. 1256), has been analyzed by Geiger: it yielded 69·09 kernel, and 23·82 husk: this quantity of husk or shell yielded, resin and bitter extract 1·91, gum 1·91, lignine 20·0. The kernel (69·09 parts) afforded, fixed oil 46·19, gum 2·40, albumine 0·5, starch with lignine 20, water 7·09.

*Rosa gallica*. Red-rose leaves contain, according to Cartier, a red coloring principle greened by alkalis, gallic acid, tannine, and albumine. From rose leaves which have been infused in water, alcohol abstracts a yellow fixed, and a volatile oil. Dried rose petals, digested in ether, yield oil, gallic acid, tannine, and coloring matter. When burned, their ash contains phosphate of potassa and of lime, carbonate of lime, chloride of potassium, silica, and oxide of iron.

*Ruta graveolens*. Rue contains, according to Knemmel, a peculiar acid. (*Chem. Gaz.*, Jan., 1843.) This is further described by Boertraeger under the name of *Rutinic acid*. (*Ibid.*, Sept., 1845.)

*Salvia officinalis*. 100 parts of fresh *sage-leaves* yield extractive (including an azotized substance and nitrate of potassa) 2·12, gum 1·51, green resin 2·9, albumine 0·43, lignine 15·87, water and loss 77·17. They also yield 0·16 per cent. of a pale yellow volatile oil; sp. gr. 0·864; soluble in alcohol, but difficultly so in ether. (ILISCH.)

*Sambucus nigra*. Elder flowers have not been minutely examined; they contain a peculiar bitter extractive, and yield, on distillation, a buttery oil, which gives flavor to *elder-flower water*.

*Saponaria officinalis*. The root of this plant, and of *Gypsophila struthium*, contain a white uncrystallizable substance which has been termed *Saponine*; it is bitter and acrid, very soluble in water, with which it forms a frothy soap-like solution; it is very little soluble in alcohol, and insoluble in ether. It has also been termed *Strutheine*. (BUSSY, *Ann. der Pharm.*, vii. 168, and *Ann. Ch. et Ph.*, li. 390. FREMY, *Ibid.*, lviii. 101. See also MALAPERT, on the occurrence of saponine in other plants. *Journ. de Pharm.*, x. 339.)

*Scilla maritima*. The bulbs of the squill contain a peculiar bitter and apparently resinous substance, called by Vogel *Scillitine*. (*Ann. de Chimie*, LXXXiii. 147.) Squill has also been analyzed by Tilloy (*Journ. de Pharm.*, xii. 635,) and by Buchner, who examined the fresh juice. (*Berliner Jahrbuch der Pharm.*, xv. 1.)

*Scorzonera Hispanica*. The fresh root of this plan contains, 9 starch, 3 resin, 10 extractive, 32 water, 46 lignine. (JUCH.)

*Secale cereale.* Rye has been analyzed by Einhof and by Greif with the following results. (JOHNSTON'S *Agricult. Chem.*, 746.)

|                | Einhof.     | Greif.      |
|----------------|-------------|-------------|
| Husk .....     | 6·4         | —           |
| Glutine .....  | 9·5         | 12·8        |
| Albumine ..... | 3·3         | 3·0         |
| Starch.....    | 61·1        | 58·8        |
| Sugar .....    | 3·3         | 10·4        |
| Gum .....      | 11·1        | 7·2         |
| Loss .....     | 5·3         | 7·8         |
|                | <hr/> 100·0 | <hr/> 100·0 |

*Secale cornutum.* The *ergot of rye*, which appears to possess such extraordinary influence in promoting the natural contractions of the uterus in child-birth, has been analyzed by Vauquelin and by Pettenkofer, but their researches throw no light upon its medical virtues. It yields a deep brown tincture to dilute alcohol, which on evaporation leaves 18·72 *per cent.* of wax, which fuses at 212°. The tincture, deprived of wax, affords a transparent brown bitter and sour extractive, which becomes moist in the air; after some days small cubic crystals form in it, which Pettenkofer suspects to be a salt of morphia, but of this there is no evidence. Water takes up a brown bitter extractive from the residue of the ergot insoluble in alcohol. The extraordinary medicinal peculiarities of ergot have been referred by Wiggers to *Ergotine*: he obtains it by digesting the pulverized ergot first in ether and then in alcohol: on evaporating the alcoholic liquor a substance remains, which, after having been acted on by water, leaves the ergotine, in the form of a bitter brown substance, insoluble in water and in ether, but soluble in alcohol, and in alkalis, and precipitable unchanged, by the acids, from its alkaline solutions. (*Ann. der Pharm.*, i. 171.)

*Sinapis alba.* The seeds of *white mustard* contain, 1. volatile oil; 2. fixed oil; 3. yellow coloring matter; 4. albumine; 5. white crystalline matter; 6. bimalate of lime; 7. citrate of lime; 8. sulphocyanide of calcium; 9. free sulphur.

*Sinapis nigra.* See p. 1566.

*Smilax sarsaparilla.* The varieties and uses of sarsaparilla root are described in pharmaceutical works. Cannobio's analysis is as follows: acrid bitter resin 2·8, gummy extract 5·5, starch 54·2, lignine 27·8, loss 9·7. The relative quantity of starch compared with that of extractive is enormously great in some species as compared with others. The average produce of the *red sarsaparilla* in *pharmaceutical extract* is 33 *per cent.* A table showing the results of the examination of several kinds of sarsaparilla, by Marquart, is given in the *Chem. Gaz.* for Aug., 1843. The extraordinary medicinal virtues of sarsaparilla are probably to be referred to the general composition of the root, rather than to any distinct principle, but as yet we have no good analysis of it. A substance called *parilline*, and afterwards *smilacine*, was first obtained from it by Pallota, (*Journ. de Pharm.*, x. 543.) which Batka afterwards termed *parillic acid*, (*Ibid.*, xx. 43,) and which, according to Theubeuf, (*Ibid.*, xx. 679,) is obtained by boiling the root in alcohol, then distilling off about one-third, digesting animal charcoal in the residue, and filtering whilst hot; the smilacine separates on cooling in the form of a white



crystalline powder, nearly tasteless, very little soluble in water or in cold alcohol, but more so in hot alcohol and in ether. Its aqueous solution is neutral, and froths when shaken. It appears to be soluble in the acids, but not to combine with them. The formula assigned to *smilacine* is  $C_{18}H_{15}O_5$ .

*Solanum dulcamara*. The stalks of this plant contain, according to Pfaff (*Mat. Med.*), 21 *per cent.* of a saccharo-bitter extract, which he terms *Picroglycion*. Its bitterness is said to be derived from *malate of solania* (p. 1454).

*Solanum tuberosum*. Several kinds of potato have been examined by Einhof and Lampadius: their composition is shown in the following table:

| Kind of Potato.         | Water. | Starch. | Gum. | Albumine. | Lignine. |
|-------------------------|--------|---------|------|-----------|----------|
| Red .....               | 75·0   | 15·0    | 4·1  | 1·4       | 7·0      |
| Sprouted .....          | 73·0   | 15·2    | 3·7  | 1·3       | 6·8      |
| Large red Surinam ..... | 78·0   | 12·9    | —    | 0·7       | 6·0      |
| Kidney .....            | 81·3   | 9·1     | —    | 0·8       | 8·8      |
| Sweet .....             | 74·3   | 15·1    | —    | 0·8       | 8·2      |
| Peruvian .....          | 76·0   | 15·0    | 1·9  | 1·9       | 5·2      |
| English .....           | 77·5   | 12·9    | 1·7  | 1·1       | 6·8      |

The quantity of solid matter in the potato varies with its state of ripeness: the ripest lose from 68 to 70 *per cent.* in drying; the least ripe from 70 to 80 *per cent.* The proportion of starch varies from 8 to 16 *per cent.* (KÖRTE.) Davy obtained from 18 to 20 *per cent.* Körte obtained, as the mean result of the examination of 55 varieties of potato, a *percentage* of 24·9 solid matter; the average of the starch was 11·85 *per cent.* (SCHÜBLER, *Agric. Chem.*) Those potatoes keep best in which starch is most abundant; but the starch diminishes, probably passing into gum and sugar, by keeping: thus, from the same variety of potato, Payen obtained 17·2 *per cent.* of starch in October, and only 14·5 *per cent.* in April. A portion of the albumine also at the same time disappears. Thus in new potatoes Boussingault found 2·25 *per cent.* of albumine (gluten), but in old potatoes only 1·5 *per cent.* (JOHNSTON'S *Lectures*, 761.) The analyses of diseased potatoes have thrown no light upon the cause of the malady, or the means of cure.

*Strychnos columbina*. *Snakewood*. It contains green fat, yellow extractive, gum, strychnate or igasurate of strychnia (p. 1444), and lignine.

*Syringa vulgaris*. The terms *syringine* and *lilacine* have been applied to a bitter crystallizable principle obtained by Meillot (*Journ. de Pharm.*, ii. 25), and by Bernays (*Buchner's Repert.*), from the leaves of this tree.

*Tamarindus Indica*. The pulp of this fruit contains, according to Vauquelin, 12·5 sugar, 4·7 gum, 6·2 jelly, 0·4 malic acid, 9·4 citric acid, 1·5 tartaric acid, 3·2 bitartrate of potassa, 36 ligneous matter, 30 water. Scheele asserts that the whole of the acid in tamarinds is the tartaric acid.

*Theobroma cacao*. This tree, as the source of the chocolate-nut, and its oil, has already been adverted to (p. 1262.) According to Woskresensky, (*Revue Scientif.*, viii. 304, and *Erdmann and Marchand's Journ.*, xxxiii. 294,) the seeds also contain a white pulverulent substance

of a bitter taste resembling caffeine, sparingly soluble in hot water, and but little soluble in alcohol or ether. This substance has been called *Theobromine*, and consists of  $C_9 H_5 O_2 N_3$ . The kernels of the cacao seeds consist, according to Lampadius, of

|                               |       |
|-------------------------------|-------|
| Fat oil .....                 | 53.10 |
| Azotized substances } .....   | 16.70 |
| Theobromine .....             |       |
| Starch .....                  | 10.91 |
| Gum and coloring matter ..... | 9.76  |
| Lignine .....                 | 0.90  |
| Water and loss .....          | 8.63  |
| <hr/>                         |       |
| 100.00                        |       |

*Tilia Europæa*. In hot seasons a saccharine secretion collects on the leaves of the *lime tree*, containing sugar, mannite, mucilage, and albumine. It has a slightly acid reaction, probably due to malic acid. (LANGLOIS. *Ann. Ch. et Ph.*, Mars, 1843.) The flowers of the *lime tree* contain, according to Pfaff, a peculiar odorous principle, which passes over in distillation with water, but cannot be separated in the form of volatile oil; but Brossat, from very large quantities of the flowers, obtained a little highly fragrant oil, lighter than water; they also contain tannine, sugar, gum, and lignine. They are well known to attract swarms of bees. When chewed, they appear very mucilaginous. Roux obtained from them, by the action of alcohol, a yellow coloring-matter.

*Triticum repens*. The root of this species of grass abounds in sugar; 100 parts of dry root (=112 fresh) yield 17 to 18 parts of an agreeable syrup. (*Mellago graminis* of foreign pharmacy.) Pfaff has rendered it probable that it contains *manna sugar*.

*Triticum vulgare*. The following table shows the composition of some varieties of French and of Odessa flour, determined by Vauquelin. (DUMAS, vi. 338.)

| COMPOSITION OF THE FLOUR OF |                |                 |                      |               |                |                 |
|-----------------------------|----------------|-----------------|----------------------|---------------|----------------|-----------------|
| FRENCH WHEAT.               |                |                 |                      | ODESSA WHEAT. |                |                 |
|                             | First Quality. | Second Quality. | Paris Bakers' Flour. | Flinty Wheat. | Soft Wheat.    |                 |
|                             |                |                 |                      |               | First Quality. | Second Quality. |
| Water ....                  | 10.0           | 12.0            | 10.0                 | 12.0          | 10.0           | 8.0             |
| Gluten ....                 | 11.0           | 7.3             | 10.2                 | 14.6          | 12.0           | 12.0            |
| Starch ....                 | 71.5           | 72.0            | 72.8                 | 56.5          | 62.0           | 70.8            |
| Sugar .....                 | 4.7            | 5.4             | 4.2                  | 8.5           | 7.4            | 4.9             |
| Gum .....                   | 3.3            | 3.3             | 2.8                  | 4.9           | 5.8            | 4.6             |
| Bran .....                  | ....           | ....            | ....                 | 2.3           | 1.2            | ....            |
|                             | 100.5          | 100.0           | 100.0                | 98.8          | 98.4           | 100.3           |

*Tropæolum majus*. By distilling *nasturtium* seeds with water, Bernays obtained a heavy acrid yellow oil, containing sulphur. When zinc and sulphuric acid were added to the distilled water, and the evolved gas passed into a solution of basic acetate of lead, sulphuret of lead was formed. (BUCHNER, *Repertorium*, xxxviii. 387.)



*Ulmus campestris.* *Elm bark* contains a green fatty matter, soluble in alcohol and ether; it is obtained by the action of water upon the alcoholic extract of elm bark, which leaves it soluble in ether. This bark also contains a peculiar gelatinous matter (a salt of pectine?) A peculiar and modified extractive oozes from elm bark, which is above described under the name of *ulmine*. Berzelius justly inveighs against the application of that term to a variety of dissimilar products.

*Valeriana officinalis.* This root contains, according to Trommsdorff, volatile oil 1·2, a peculiar extractive, 12·5, gum 18·75, an odorous soft resin 6·25. The essential oil is the source of the odor. 100 lbs. of clean valerian root yield between 38 and 39 of *pharmaceutical extract*. (See p. 1552.)

*Vanilla aromatica.* The pods of this plant give a peculiar perfume to creams, chocolate, and confectionary. They yield no volatile oil when distilled. The white acicular crystals found upon them are said to be a concrete volatile oil; but Bucholz found benzoic acid in them, and more than 10 per cent. of a fat oil. (*Buchner's Repert.*, ii. 253.)

*Variolaria amara.* A peculiar bitter principle, *Picrolichenine*, has been extracted by Alms from this lichen; it is crystallizable, and has some peculiarities as a coloring-matter under the influence of ammonia. (*Ann. der Pharm.*, i. 61; LÖWIG, i. 817.)

*Veratrum album.* *White Hellebore.* See *Veratria* (p. 1450.) The root contains a peculiar fatty matter, yellow extract, gallate of veratria, gum, starch, and lignine.

*Vicia Faba.* *Garden Bean.* This species, commonly known as *broad Windsor*, or *field bean*, contains, according to Einhof,

|                             |             |
|-----------------------------|-------------|
| Water .....                 | 15·6        |
| Husk'.....                  | 10·0        |
| Legumine, albumine, &c..... | 11·7        |
| Starch .....                | 50·1        |
| Sugar.....                  | 8·2         |
| Gum .....                   |             |
| Oil and fat)                |             |
| Salts and loss .....        | 4·4         |
|                             | <hr/> 100·0 |

*Vitex Agnus castus.* The seeds contain a bitter crystallizable substance, called by Landerer *Castine*.

*Vitis vinifera.* The juice of sour grapes only contains tartaric acid. The juice of the ripe grape contains odorous matter, sugar (p. 1184), gum, albumine, a trace of malic acid and malate of lime, free tartaric acid, tartrate of lime, and bitartrate of potassa, (also racemic acid?)

*Wintera aromatica.* *Winter's canella bark.* It contains an acrid volatile oil, mild resin, colored extractive, a peculiar kind of extractive and of sugar, gum, starch, albumine, lignine, and several salts. (HENRY, PERSOZ, and ROBINET.)

*Xanthorhea hastilis.* (*Acarois resinifera*.) This tree grows abundantly in New Holland, especially near Sydney; it yields the substance known in commerce under the name of *yellow gum*, or *acaroid resin* of Botany Bay (p. 1576;) it is of a deep reddish-yellow color, and when heated emits a fragrant odor like that of balsam of tolu. It con-

tains cinnamic and benzoic acid. (STENHOUSE, *Mem. Chem. Soc.*, iii. 10.)

*Xanthoxylum Caribæum*. (*X. clava Herculis*.) The bark of this tree is used in the Antilles as a febrifuge. Chevallier and Pelletier found in it a peculiar principle, which they termed *xanthopicrite*: it is soluble in water, very soluble in alcohol, insoluble in ether; it forms yellow silky crystals, and is very bitter and astringent; it has no alkaline reaction; animal charcoal extracts it from its aqueous solution, and hot alcohol extracts it again from the charcoal. (*Journ. de Chim. Med.*, ii. 314; *Ann. Ch. et Ph.*, xxxiv. 200.)

*Zea mais*. According to Gorham, *maize*, or *Indian wheat*, contains starch 77, *zeine* 3, albumine 2·5, sugar 1·45, extractive 0·80, gum 1·75, sulphate and phosphate of lime 1·5, lignine 3, water 9. According to Bizio, *zeine* contains nitrogen as an ultimate element: Gorham regards it as without nitrogen. Dry maize has been analyzed by Payen, who gives the following results, but there is probably some mistake in regard to the fat:—

|                      |       |
|----------------------|-------|
| Husk .....           | 5·0   |
| Glutine .....        | 1·2   |
| Starch .....         | 7·1   |
| Sugar and gum .....  | 0·5   |
| Fatty matter .....   | 8·9   |
| Coloring matter..... | 0·05  |
| Salts .....          | 1·8   |
|                      | <hr/> |
|                      | 24·55 |

According to Dumas, the fatty matter only amounts to 8·9 *per cent.* in maize, and according to Liebig, only to 5 *per cent.*

## § XV. VINOUS FERMENTATION. ALCOHOL. ETHER.

THE term *vinous fermentation* is employed to signify the spontaneous changes which certain vegetable solutions undergo, placed under certain circumstances, and which terminate in the production of an intoxicating liquor. The principal substance concerned in vinous fermentation is *sugar*; and no vegetable juice can be made to undergo the process, which does not either originally contain it, or some other principle, such as starch or dextrine, capable of being converted into sugar. In the production of *beer*, the sugar is derived from the *malt*; in that of *wine*, from the juice of the *grape*.

**BEER.** This beverage is first mentioned by Herodotus, (who was born 444 years before the commencement of the Christian era:) he informs us that it was the ordinary drink of the Egyptians, and that it was made from barley, because vines did not grow in their country. (*Euterpe*, c. 27.) According to Tacitus, beer was in common use with the Germans as early as the first century of the Christian era (*De Moribus Germanorum*, c. 23), and it is mentioned by Pliny, as employed in Spain, and in Gaul, under the name of *cerevisia*. (*Nat. Hist.* lib. xxii. c. 25.) In Europe, beer is almost exclusively made from



barley which has undergone the process of *malting*, so as to convert it into *barley-malt*.

*Malt* is the grain of barley which has been made to germinate to a certain extent, after which the process is stopped by the application of heat. For this purpose the barley is first steeped in cold water for a period of about forty hours, during which it swells, in consequence of the absorption of moisture, and increases about 50 *per cent.* in weight, and about one-fifth in bulk; 100 pounds of barley producing 150 pounds, and 100 bushels, 120. The steep-water acquires a yellow color, and holds in solution a peculiar bitter extractive matter derived from the husk of the grain, and varying in quantity, from one-hundredth to one-fiftieth of the weight of the barley. After the barley has remained a sufficient time in the steep, the water is drained off, and the grain is thrown upon the malt-floor, where it is formed into a rectangular heap about sixteen inches deep, called the *couch*, which, after about twenty-six hours, is turned by wooden shovels, and somewhat diminished in depth. This turning is frequently repeated, and the depth of the heap gradually reduced. The seed now begins to germinate, and absorbing oxygen, evolves carbonic acid; its temperature gradually increases, and in about ninety-six hours is 8 or 10 degrees above that of the surrounding air; and now, the grain, which had at first dried, becomes again moist upon the surface, and exhales an agreeable apple-like odor: this is called *sweating*. By frequently turning the malt at this period, it is kept at a proper temperature, which varies from 60° to 70°. At the period of the sweating, the rootlets of the grain begin to appear, and about a day afterwards, the future stem, called *acrospire* by the maltsters, is visible; it rises from the same extremity of the grain with the root, and advances within the husk towards the opposite end, but the process of malting is stopped just before it begins to protrude. During this incipient vegetation, the grain becomes white, and mealy, in consequence of the developement of *diastase* (p. 1170), which would again gradually disappear if the germination were to continue, so that it is stopped, at this period, by drying the malt upon the *kiln*, where its temperature is gradually raised to about 140°, or somewhat higher. A part of the starch of the grain is already converted into dextrine and sugar (p. 1170), and the whole of it is in general so far changed as to become red, instead of blue, by the action of iodine. According to Dr. Thomson (*Veg. Chem.* 1013), barley, by conversion into malt, increases 2 or 3 *per cent.* in bulk, and loses, upon an average, about one-fifth of its weight; but, of these 20 parts *per cent.* 12 are to be ascribed to kiln-drying, and consist of water, which the barley itself would have lost had it been exposed to the same temperature; so that the real loss amounts to about 8 *per cent.* (See note, p. 1170.) When the malt is dried, it is ground, and is then fit for the use of the brewer. Malt which has not been exposed to a temperature beyond 140°, is designated *pale malt*, and is in the best condition for the production of beer; but color and flavor are derived from malt which has been more highly dried. *Yellow*, or *amber malt*, has been dried at about 200°, and from that upwards, according to color. What is termed *brown*, or *blown malt*, has been exposed to a yet higher temperature, namely, from 280° to 300°, and though not fermentable, in consequence of its *diastase* having been destroyed by heat, it gives a peculiar tint and

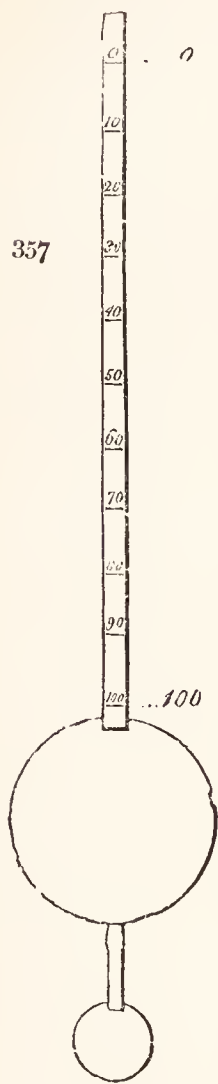


taste to the beer; and, lastly, malt which has been *parched*, so as to constitute *high-dried*, *roasted*, or *black malt*, is almost exclusively used to communicate to porter its very dark-brown color. To a good liquor, brewed from pale malt, any depth of tint may be communicated by the careful use of roasted malt, which, when genuine and carefully prepared, is an unexceptionable coloring-matter, but caramel or burned sugar would probably be preferable, if its use were not illegal. The characters of good *pale malt* are as follow: it is plump, and when crushed appears full of white pulverulent starch; it has an agreeable odor, and a sweet taste, and may be easily chewed into a pasty mass. It floats upon water, whereas the unmalted barley sinks. When finely ground, and rubbed up with water at the temperature of  $160^{\circ}$ , it should almost entirely dissolve, leaving little else than its husk or pellicle.

*Wort.* This term is applied to the liquor resulting from the action of hot water upon the malt; the process by which this infusion or liquor is obtained, is called *mashing*, and the vessel used for the purpose is the *mash tun*. The construction of this and the other vessels, together with their dimensions, and details respecting the mechanism of the brewery, are given in URE'S *Dictionary of Arts, &c.* The object of *mashing* is to extract the saccharine matter of the malt, and to convert its unchanged starch into dextrine and sugar, by the action of the diastase; and in order to effect these changes, great attention must be paid to the temperature at which the operations are carried on; for if it be inadequate, the conversion will be sluggish and imperfect, and if too high, an intractable magma will be formed, which cannot again be brought into a proper state of solution. The best temperature for these purposes is from  $160^{\circ}$  to  $165^{\circ}$ , and the quantity of water used in the first instance should be about equal to the bulk of the malt; the larger the proportion of water, the more complete is the formation of sugar; an insufficiency of water inducing a greater production of dextrine. For the first mashing, the temperature of the water should not exceed  $165^{\circ}$ , for if above that point, the diastase is so modified as to lose much of its efficiency; and it is advantageous to let the water flow upon the malt in the first instance at  $140^{\circ}$ , which is sufficient to dissolve the sugar already formed in the grain, and to soften and inflate the starch, and when this has been done, a quantity of water at about  $190^{\circ}$  may be added, so as to establish a mean of about  $165^{\circ}$ . The mashing is then proceeded with; that is, the hot water and malt are well blended by continuous stirring, and afterwards left covered for two or three hours, when the clear wort is drawn off by a cock at the bottom of the mash-tun; this vessel generally being provided with a perforated, or false bottom, so as to prevent the flowing out of the residue of the malt. By this first operation nearly the whole of the starch is saccharized, so that water of  $195^{\circ}$  may now safely be used for the second mashing, which, flowing on the malt, will be reduced to about  $180^{\circ}$ ; this second operation is conducted in the same manner as the former, and the second wort is added to the first. A third mashing may then be performed at a still higher temperature, namely, with water at about  $200^{\circ}$ , so as to remove all soluble remains from the malt, leaving nothing but husk or ligneous fibre, a small portion of coagulated albumine, and minute portions of other foreign matters; this residue, under the name of *brewers' grains*, being used by the London cow-keepers as



food for their cattle. This third and meagre infusion is not generally mixed with the others, but is used in the production of *London small beer*; or where that article is not prepared, it is employed instead of water in the next mashings. The quantity of wort obtainable from a given quantity of malt will of course in a great measure depend upon the nature of the beer to be brewed. Its strength is frequently adjusted by its density, which is determined by an instrument not quite correctly called a *saccharometer*, since it is influenced by all the contents of the wort, and not by the sugar only. It is a brass instrument, resembling the common hydrometer, of the shape shown in the margin, and so adjusted in weight as to sink to the point marked 0°, in distilled water at the temperature of 70°, and when immersed in a liquor of the same temperature, and of the specific gravity of 1.100, it is buoyed up to the mark 100, just above the bulb. The intermediate space is divided into 100 parts, so as to indicate intermediate degrees of specific gravity. This is the simplest and most useful form of the instrument, though not that in common use. Brewers employ complicated and often unmeaning terms to designate the strength of their worts, and speak of the proportion of *saccharine per barrel*, &c. A reform in this department of their business, by the introduction of a new instrument, and of tables showing the quantity of solid matter in worts of given density, and expressed in reference to specific gravity only, would be desirable.



The specific gravity of the wort for *ale* is usually about 1.090 to 1.100, and for *table beer* (properly so called) from 1.020 to 1.030.

*Hops.* The wort is next boiled with *hops*, which are the strobiles or catkins of the *Humulus lupulus*, a diœcious plant belonging to the nat. ord. *Urticaceæ*, the culture of which was introduced into this country from Flanders, in the reign of Henry VIII. (BECKMAN'S *Hist. of Invent.*) Hops consist of scales, nuts, and lupulinic grains or glands. The *scales* are the enlarged and persistent bracts which enclose the nuts. The *nuts* are small, hard, nearly globular, and covered with aromatic superficial globose glands. The *lupulinic glands* or *grains*, commonly termed *yellow powder* or *lupuline*, are the most important part of the strobiles. According to Ives, dry hops ought to yield about one-sixth of their weight of this yellow granular powder. (*Journ. of Science*, xi. 205.) According to Payen and Chevallier (*Journ. de Pharm.*, viii. 209), the principles contained in this active part of the hop, are volatile oil, bitter extractive, resin, and gum. Sulphur, silica, acetate of ammonia, chloride of potassium, sulphate and malate of potassa, phosphate and carbonate of lime, and oxide of iron, are also present. (See also p. 1619.) A very important part of the management of the hop consists in the mode of drying it, which is performed in drying kilns, termed in Kent and Sussex *oast houses*: they are generally very unscientifically constructed, and would apparently admit of easy and important improvements. In order to obtain a proper marketable color, the hops are here subjected to fumi-

gation with sulphurous acid, and are finally packed into sacks, or pockets, in which they are subjected to great pressure, so as to prevent the access of air, and their consequent deterioration. They should have a golden-yellow tint, and a strong and peculiar aromatic odor, and should be kept as far as possible excluded from air, and in a dry warehouse.

The relative proportion of hops used in beer varies considerably according to the desired qualities of the liquor; about one-twentieth of the weight of the malt is said to be generally employed. They diminish the tendency of the beer to subsequent fermentation, and other changes by keeping, and by their aromatic bitter they cover the sweetness, and impart a new odor and flavor to the liquor, and as these qualities are in part referable to the volatile oil of the hop, the boiling should be as short as possible, and the boilers so constructed as to dissipate the least possible quantity of aroma.

When the wort is sufficiently boiled, it is drawn off and strained from the hops, and is then generally thrown into large and very shallow vessels, termed *coolers*, which are ranged, one above the other, in the most exposed part of the brewery, so that by evaporation, radiation, and currents of air, which are sometimes artificially obtained by means of revolving fans, the original temperature of the hot liquor, which is about  $160^{\circ}$  to  $180^{\circ}$ , may be brought down, as rapidly as possible, to  $60^{\circ}$ , or even lower. This cooling process is sometimes aided by *refrigerators*, the hopped wort being passed through thin copper tubes or hollow plates, surrounded by larger tubes conveying a current of cold water in the opposite direction. When duly cooled, the liquor is let into the *fermenting vessels* or *gyle tuns*, which must be of adequate dimensions to contain the worts and leave at least six or eight inches of the depth unoccupied; they also usually have a framework and loose boarding on the top, to receive the rising head of froth. A sufficiency of *yeast* having been added, fermentation comes on in the course of six or eight hours; a white foam collects upon the surface, the temperature of the liquor rises, and carbonic acid escapes in gradually increasing quantity: at length the evolution of gas ceases, the liquor becomes quiet and clear, and it has now lost much of its sweetness, has diminished in density, acquired a new flavor, and become *intoxicating*, in consequence of the generation of alcohol. In our large breweries, where enormous quantities of material are operated on, many other processes are adopted which will be found described in the works I have elsewhere quoted, and a peculiar system of management is had recourse to, in reference to what may be called the *finishing* of the beer; namely, the separation of the yeast, the conclusion of the fermentation, the fining, and the storing and ripening and further treatment of the liquor. But all these matters can only be well understood in the breweries themselves, which must be visited in order to form a just conception of the ingenuity of the machinery, and the enormous magnitude of the operations. Those who are curious in the history of *ale* and *porter*, will find the various additions which are said to be made to those liquors prescribed in various "Treatises on Brewing." *Porter* derives its peculiarities from *high-dried* malt, a certain proportion of which is used in the wort; it is also colored with *parched* malt, or other coloring materials. As issued from the large breweries, it is a genuine and excellent liquor, but it is generally adulterated and deteriorated by the *publicans*.



A species of beer, or rather, substitute for beer, is made in Russia, which is called *quaas*: 9 parts of rye-meal, and 1 of undried rye-malt, are made into a paste with water, and left for some days in a warm place, when the mass becomes quite sweet: a wort is then prepared from it, which is run off into casks, where by the addition of a little yeast, it is brought into slow fermentation; when this terminates it is ready for use.

The components of beer are

|                  |                       |
|------------------|-----------------------|
| Water.           | Glutine or Albumine.. |
| Alcohol.         | Fatty matters.        |
| Sugar (Glucose). | Essential oil.        |
| Gum (Dextrine).  | Carbonic acid.        |
| Extractive.      | Salts.                |

The proportion of alcohol (sp. gr. 0·825 at 60°) in different samples of ale, porter, and table beer, fluctuates from between 8 and 9, to between 1 and 2 *per cent.*, by measure. (See *table*, p. 1646.) The average amount of such alcohol in the common varieties of *London ale*, is about 6 *per cent.*; in *porter*, about 5 *per cent.*; and in *small beer*, about 1 *per cent.* The quantity of solid matters in the better kinds of beer varies from about 4 to nearly 8 *per cent.* An imperial pint of good porter yields in general about an ounce and a half of extract. The fattening tendency of strong beer has sometimes been referred exclusively to the oily or fatty matters which it contains; but Vogel has shown (*Ann. der Pharm.*, May, 1843) that a quart of strong beer (Munich winter-beer) contains only about 1·75 grains of fatty matter in the 18 drachms of extract which it yields on evaporation; supposing, therefore, two quarts of such beer to be taken daily, the annual amount of fat from that source would be about two ounces and a half, a quantity by no means adequate to account for the frequent corpulence of beer-drinkers, and which therefore must be attributed to other causes.

Although in the ordinary proceedings of the brewery *yeast* is always added to accelerate the commencement and progress of fermentation, which in our large establishments is usually completed in three or four days, it is by no means a necessary addition, inasmuch as there is abundance of ferment contained in the wort itself, but not in that *state of change* which tends to produce rapid fermentation; this ferment, however, separates during the process, and is, in fact, the source of yeast itself. But excellent beer may be brewed without the use of yeast; the wort having been boiled as usual with the hops, and cooled down to about 80°, may be at once transferred, hops and all, into a cask set on end and made air-tight, except that a piece of pewter tube is adapted by a bung to the head of the cask, to allow of the escape of carbonic acid; this tube should be sealed, by dipping into a cup of wort. The fermentation, in a cellar not too cold, will come on in a day or two, and proceed regularly and sometimes rather violently, for a fortnight or three weeks; when it ceases, the escape tube is to be removed and the aperture perfectly closed by a peg: the beer gradually fines, and may then be drawn off for use; the hops, insoluble yeast, and other matters, partly float upon the surface and partly sink to the bottom. There should therefore be two cocks to the cask; one, on a level with the usual bung hole, and the other within a few inches of the bottom, so as to admit of the beer being drawn off fine, first by the upper, and then by the lower tap. The



beer resulting from this mode of proceeding is of excellent quality; it generally has a more vinous flavor than common beer, and may be kept at tap for months without acescence.

In this case, and also in the ordinary mode of brewing, the carbonic acid which escapes during fermentation always carries traces of carbonate of ammonia with it, which may be detected in the water through which the gas has bubbled. The ammonia probably arises from the decomposition of part of the gluten and other azotised principles of the wort and yeast during the process of fermentation. Many years ago experiments were made at Messrs. Combe and Delafield's brewery, for the purpose of determining the nature of the products passing off, along with the carbonic acid, from the fermenting gyle, which was so constructed as to convey them into a kind of Woulfe's apparatus (p. 317); alcohol, essential oil, and carbonate of ammonia, were thus obtained, but not in sufficient quantity to render the process economically or usefully available. A similar mode of conducting the fermentation has been recently suggested by Furze. (*Mem. Chem. Soc.*, ii. 21.)

WASH. The distillers prepare a liquor called *wash*, for the express purpose of producing from it ardent spirits\*; instead of brewing this from pure malt they chiefly employ raw grain, mixed with a small quantity only of malted grain; the water employed in the mash-tun is generally used of a lower temperature than that adopted in brewing beer, and the mashing is longer continued. The wort is afterwards fermented with yeast, and then distilled, with further precautions afterwards to be noticed in reference to the production of proof spirit and alcohol.

WINE. *Wines* properly so called are exclusively derived from the juice of the grape, which, when expressed from the ripe fruit, is termed *must*; it holds many substances in solution, the principal of which

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\* The operations of our distilleries would be improved by an alteration in the excise laws: as these at present stand, the duty is charged from calculations, 1. On the quantity and density of the *wash*; 2. On the quantity and density, or strength of the *low wines*, or first products of distillation; 3. Upon the quantity and strength of the *spirit*, or, in other words, of the *alcohol* actually produced: it is presumed, in reference to the *wash*, that the alcohol which it will afford by fermentation will be directly as its *density* (without reference to the *nature* of the matter which it holds in solution). In the *low wines*, and in the *spirit*, the proportion of alcohol is inversely as the density, and the duty is charged in conformity with experiments upon the composition of mixtures of alcohol and water of different densities. I say nothing here of the mode of judging of the value of the wort by its *attenuation* during fermentation, nor of the fallacies to which the different operations are liable, and am aware of the

danger and difficulties of meddling with so important a branch of the revenue; but no scientific person can visit a distillery without at once seeing much that is susceptible of safe and effectual alteration; or peruse the multitudinous documents, and evidence brought before the Commissioners of Revenue Inquiry, and before Parliamentary Committees, bearing directly or indirectly upon this subject, without hoping that some remedy may be found for the evils there set forth. In every point of view, two things seem desirable, and apparently not unattainable; the one, that the materials employed as sources of spirit, and the mode of conducting the operations of the distillery, should be, as far as possible, unshackled; the other (a necessary consequence), that the duty should be levied upon the *ultimate produce at the worm-end*, or, in other words, upon the *quantity of absolute alcohol* actually produced, and that the charge should be made in reference to that alone.



are *glucose* or *grape sugar*, *starch* and *gum*, *albumine* and *glutine*, *tannine*, *extractive* or *coloring-matter*, *bitartrate of potassa*, and *malic acid*, with a little *citric acid*: some other salts are also present, such as *tartrate of lime*, *tartrate of alumina and potassa*, *sulphate of potassa*, *chloride of sodium*, and *chloride of potassium*, and in certain grapes there are *racemates* or *paratartrates* (p. 1335), which probably replace the tartrates. Traces of an *oily matter* are also to be found in must, derived either from the juice itself, or from the seeds or from the husk of the grape; they are important in reference to the subsequent development of the odor and flavor, or *bouquet*, as it is termed, of the wine, as will appear when speaking of *œnanthic ether*.

The grape sugar, or glucose, is the source of the *alcohol* of the wine, or of its *vinosity*; the other substances are important accessories, in reference to the flavor and other characters of the numerous varieties of wine. The proportion of the sugar is judged of by the density of the must; hence the use of the hydrometer, or, as it is sometimes termed, the *mustimeter*, in its determination; but as other substances than sugar affect the specific gravity of the must, it is not always a safe guide. In bad seasons there is deficiency of sugar, and consequent diminished density of the must, and in such cases a quantity of sugar is added to it; and it has been found, that the addition of *grape sugar* or glucose (prepared by the action of dilute sulphuric acid upon starch, p. 1172,) is preferable to the use of cane sugar. It was formerly supposed that the deficiency of sugar in the grapes might be adequately compensated for by the subsequent addition of alcohol to the wine, but a much better result is obtained by the use of sugar in the first instance, in such proportion as to raise the quality of the must to its average composition in favorable seasons; and in these cases not only should starch sugar be preferred to cane sugar, but probably *grape sugar* itself would be preferable to either. (See DUMAS, *Chim. app. aux Arts*, vi. 484.)

It has been stated, in reference to the production of *beer*, that in the ordinary mode of brewing, the addition of yeast is requisite, for the purpose of accelerating the fermentation; but, as respects *grape juice* or must, no such help is wanted, and it enters at once into vinous fermentation, when its temperature is sufficiently high, namely, about 70°; so that a *ferment* must pre-exist in the juice; it is, in fact, the *albumino-glutinous* substance which answers this purpose. But a question here arises, namely, why the juice of the grape does not ferment in the fruit itself? We know that ripe grapes, even cut from the vine, exhibit no such tendency; they dry up and shrivel, becoming ultimately *raisins*, but never fermenting so long as the skin is entire. It was once supposed that this arose from the *gluten* or *ferment* being in distinct vesicles or cells from those containing the *saccharine juice*, and that consequently no fermentation could ensue till the fruit was mashed or broken so as to mix these ingredients. But Gay-Lussac found that when bruised grapes were carefully *excluded from air*, no change ensued; but that even a momentary exposure of the pulp to air or oxygen, was enough to communicate to it the power of fermentation. The action of oxygen therefore on the azotized principles of the grape, appears to confer upon them the properties of yeast. It is curious how perfectly the exclusion of *air* is provided for by the natural texture of the grape, which does not allow

its ingress, although it admits of the transpiration of *aqueous vapor*, as is shown by the spontaneous desiccation of the berry.

If we compare the proximate constituents of *wine* with those of *must*, we find, in the first place, that a great part of the sugar is converted into alcohol, and that certain substances soluble in the original must, are no longer soluble in the vinous liquor. The leading components of wine are *water*, *alcohol*, *sugar*, *gum*, *extractive matters*, *azotized matter*, generally regarded as *albumine*, *bitartrate of potassa*, *tartrate of lime*, *tartrate of alumina and potassa*, *sulphate of potassa*, *chloride of potassium*, and *chloride of sodium*. In red wine there is a red coloring-matter, and generally *tannine*; and in champagne and other sparkling wines, a large quantity of *carbonic acid*. There is also, in all wines, more or less of an *odorous principle*, partly derived directly from the grape, and partly formed by fermentation; it has some of the characters of an essential oil; it constitutes the *perfume* or *bouquet* of the vine, and in some cases is very evanescent and small in quantity, in others more persistent and abundant. The odorous substance formed in the process of fermentation, is represented by Pelouze and Liebig (*Ann. Ch. et Ph.*, Lxii. 439, and Liii. 115) as a true *ether*, that is, as a combination of *oxide of ethyle* with *œnanthic acid*. The formula  $C_{14}H_{13}O_2$  is represented as that of œnanthic acid, which,  $+ C_4H_5O$ , gives  $C_{18}H_{18}O_3$  as the composition of œnanthic ether. Deleschamps first separated this ether from the wines of Burgundy, and it was afterwards recognized, together with amylic alcohol (potato-spirit oil), in the products of the distillation of the grape-stalks of Montpellier. According to Laurent, these odorous compounds constituting the aroma of wines, have their origin in the fatty acids of the grape, which are converted by oxidizement into more powerful acids, and consequently more disposed to form ethers; and more volatile, and therefore calculated to affect the odor and flavor of the wine.

With very rare exceptions, the *colors of wines* are derived not from the pulp, but from the skin or husk of the grape; it acquires solubility in proportion as alcohol is developed during fermentation, and, originally blue, is then reddened by the acids of the pulp. The husks, as well as the seeds of the grape, also contain tannine, giving an astringency to the wine, and the property of acquiring a dark color in the presence of salts of iron. According to Dumas, white wines are sometimes converted into red, by the addition of coloring and astringent substances; amongst which he mentions elder berries, beet-juice, brazil wood, and logwood. Rhatany root is also said to be in request in reference to the manufacture of port wine. Vogel, Berzelius, and Nees von Esenbeck, have described the means of detecting these falsifications. According to the latter chemist (as quoted by Dumas), the following is a useful test: 1 part of alum is dissolved in 11 parts of water, and 1 part of carbonate of potassa in 8 parts of water; the wine is then mixed with an equal volume of the solution of alum, and a sufficiency of the alkaline solution gradually added, so as to precipitate the whole of the alumina, which falls in combination with the coloring-matter, in the form of a *lake*, the tint of which varies with the nature of the coloring-matters, and which also assumes, under the influence of excess of potassa, a new and distinctive hue from each coloring-principle; so that by thus treat-



ing a wine known to be genuine, and comparing the results with those derived from wines of a suspicious character, the colors of the resulting precipitates will generally be a useful guide. (In reference to the coloring-matters and other constituents of wines, see also LABADIE, *Reponses aux Questions de CHAPTAL*, &c. *Annales de Chimie*, xxx. 113 and 225.) Some *white wines*, Sauterne and Barsac especially, and I think some of the Rhenish wines, become brown or even blackish, after a few hours' exposure to air, which arises either from the presence of some modification of tannine, or from their containing, together with that principle, a trace of some protosalt of iron, which, by the action of the air, becomes peroxidized, and gives the color. The yellow or brown color of what are called *white wines*, arises chiefly from extractive matter; it is also frequently artificial; the greater part of *brown sherry*, for instance, is tinted by burned sugar.

Almost all wines contain a *free acid*, or, at least, redden litmus paper. This may merely depend upon bitartrate of potassa; but traces of acetic acid are also generally present, derived from the oxidizement of the alcohol; and frequently the effect is chiefly referable to carbonic acid, as in the effervescent wines. The effervescence observed on adding carbonate of potassa to wines, is generally caused by the bitartrate of potassa; and when a precipitate ensues, it is carbonate of lime, resulting from the decomposition of the tartrate of lime present in the greater number of instances. Some wines appear to contain malic acid. According to Berzelius, the wines of Germany frequently contain tartrate of alumina and potassa; and the same salt has been detected in the wines of Bordeaux; so that the discovery of alumina in a wine is no proof, as has sometimes been supposed, of its having had alum added to it. The presence of sulphuric acid (in the form of sulphates,) in many wines, is recognised by the formation of an insoluble barytic precipitate.

The change which wine undergoes *in the cask* is sometimes connected with a continuance of the fermentation, during which it deposits *tartar* in combination with a peculiar glutiniferous extractive and coloring-matter, the terms *red* and *white tartar* being applied to its varieties: the solvent power of the wine over tartar diminishes in proportion to the alcohol which it contains, so that the strongest wines are always in this respect the least acid. In cask, too, the wine is changed by evaporation, and the pores of the wood seem to admit of the passage of *aqueous* vapor, whilst, as is the case with bladder, they oppose the transpiration of *alcoholic* vapor; so that, whilst wine in the wood diminishes in bulk, it probably increases in strength. *In bottles* the same changes continue as in the cask, but they are extremely slow and imperfect; the wine, however, deposits its crust of extractive and tartar: and it is not uncommon to find in many wines, which have been long in bottle, crystals of tartar, and also of bitartrate of lime, the proportion of all which varies in different wines, and in the same wine according to the time which it had previously been kept in the cask. Another character of wine, which is also much influenced by its age in bottle, is that refined and delicate flavor and odor, above alluded to under the term *bouquet*, or perfume, and upon which so much of the excellence and consequent value of some kinds of wine depends.

There is no apparent limit to the time for which some wines may be



kept, not only in a perfect, but apparently in an improving state, in bottle; such especially are *madeira* and *sherry*. Many of the red wines go on for a time improving, in consequence of the deposition of extractive, tannine, and tartar; they then deteriorate, losing color and flavor; this is generally the case with *port*. The aroma or bouquet of *claret* is much improved up to a certain point, and is then apt gradually to decline; yet the deposit from that wine, or the apparent change which it suffers in bottle, is remarkably small: I have seen it after twenty-five years to have deposited nothing more than a very thin transparent film of coloring extractive, nearly equal on the whole of the interior of the bottle, together with a slight sediment of the bitartrates of lime and potassa. Some of the rich sweet wines acquire a flavor slightly resembling that of acetic ether after remaining many years in bottle, and during this change they become less and less saccharine.

Wines are liable to certain *diseases*, as they are termed, (*maladies des vins*), some of which admit of remedy. Thus, it occasionally happens that a secondary fermentation is set up in the wine in cask, which if allowed to continue, would destroy the whole of the saccharine contents of the wine, and terminate in the production of a bitter flavor. This condition of the wine may be checked by transferring it into a cask in which sulphur has been burned. The addition of sulphate of lime to the wine is also said to produce the same effect; and sometimes mustard seed is resorted to as a remedy.

Wines which are deficient in tannine, sometimes become viscid or ropy, a disorder frequently observed in champagne, and depending, according to Dumas, upon the mutual action of sugar and glutine. The best remedy in these cases is to precipitate the azotized matter by pure tannine. When wines are acid in consequence of the presence of excess of tartaric acid, the evil is remedied by the use of neutral tartrate of potassa, which throws it down in the form of tartar. The bitterness which old wines acquire as a consequence of the destruction of the whole of their sugar is remedied by the admixture of new wine more abundant in sugar. The musty flavor which wines acquire from a mouldy cask, and which is sometimes termed *tasting of the cask*, is very difficult of effectual cure. A very small addition of very pure and carefully prepared animal charcoal sometimes answers the purpose, but with red wine it is apt to affect the color. Sometimes the mustiness may be removed by agitating the wine with a very small addition of extremely pure and tasteless olive oil; it appears to absorb the essential oil, to the presence of which the mouldy flavor has been ascribed. When a cask has been made of wood which has been kept in the neighbourhood of an ant's nest, it becomes impregnated with a matter which communicates a musty flavor to the wine.

The *quantity of alcohol* contained in different wines, is very variable; the best mode of determining it consists in carefully distilling a given measure or weight of the wine, until from one-half to three-fourths have passed over, having previously neutralized the acid of the wine by a little soda, potassa, or lime. A quantity of distilled water is then added to the portion of the wine which has gone over, so as accurately to make up the original volume of the wine; the mixture is well shaken and set aside for a day or two in a stopped bottle, so that it may obtain its



maximum density; its specific gravity is then taken in the usual way, and from that datum, the proportion of alcohol (either of sp. gr. 0·825 at 60°, or as absolute alcohol), may be determined by reference to Gilpin's tables (*Phil. Trans.*, 1794), or to others which shew the quantity of absolute alcohol contained in diluted alcohol of different densities, which tables are referred to further on (p. 1659). There is, of course, no direct relation between the original density of the wine and its alcoholic content, inasmuch as some of the most alcoholic wines are also those which have the highest specific gravity, in consequence of the sugar, extract, and other substances which they also hold in solution.

It was once supposed that the alcohol obtained by the distillation of wine did not altogether pre-exist as such in the wine, but that a part of it, at least, was formed or in some way generated, in the act of distillation; that it, in fact, was a *product*, and not an *educt*. This opinion was adopted by Fabbioni (*Arte di fare il Vino*, Florence, 1788, and *Annales de Chimie*, xxx. 220), in consequence of his not being able to separate alcohol from genuine wine by means of carbonate of potassa; whereas when a little alcohol had been previously added to the wine, the portion so added was readily separable. But the fact is that alcohol may be thus separated from all wines, especially if the precaution be in the first instance taken of precipitating the coloring-matters, and acid, by the addition of subacetate of lead, or of finely pulverised litharge; the filtered wine then readily yields all its alcohol on the addition of carbonate of potassa. But there are other proofs that the alcohol obtained from wine is not *formed* in consequence of the high temperature generally resorted to for its distillation; for in the first place the quantity of alcohol so procured from any wine is the same at whatever temperature it be distilled; and when distilled *in vacuo* at the temperature of 60°, the produce of alcohol is the same as if distilled at its boiling-point. We may therefore safely assume, that the proportion of alcohol yielded by distilling a wine, is that which was pre-existent in the liquor. But, as the percentage of alcohol thus obtained, is in many instances very large, it has been assumed, that although pre-existent in the wine, it must be contained in it in some peculiar state of combination, inasmuch as any given quantity of wine is apparently less heating and intoxicating, than the same quantity of a mere *mixture* of alcohol and water of the same strength: that a wine, for instance, containing 20 *per cent.* of alcohol, is less inebriating than brandy-and-water of the same alcoholic strength. This is perhaps to a certain extent true, inasmuch as when strong alcoholic liquors are mixed with water it is many hours before they thoroughly combine, or before that mutual penetration of the two liquors ensues which will be afterwards adverted to, and which is attended by a proportionate increase upon their mean density; the presence, too, of acid, extractive, astringent, saline, and some other matters in the wine may tend to blunt the inebriating and stimulating powers of its alcohol; but after all it does not appear that the effects of wine as opposed to those of diluted spirituous liquors, are much at variance, provided the latter have had time to attain their maximum density; the evils of dram-drinking not arising so much from the absolute quantity of alcohol swallowed, as from its state of concentration. No doubt, however, a difference does exist between wine, and alcoholic mixtures of the same strength as

The following table shows the quantity of alcohol *per cent.*, *by measure*, contained in different wines and other liquors. My own results, and those of Dr. Prout, and of J. Fontenelle, refer to alcohol of the specific gravity of 0·825 at 60°; that is, to alcohol consisting of 89 *per cent.* by weight of *absolute alcohol* (sp. gr. 0·796 at 60°), and 11 of water. Dr. Christison's results, and those of Ziz, have reference to *absolute alcohol*. (See HENDERSON *on Wines*, p. 361. PEREIRA *On Food and Diet*, p. 157.)

|   | Alcohol<br>(sp. gr. 0·825<br>at 60°)<br>per cent.<br>by measure. | Sp. gr.<br>of the<br>Wine. | Authority. |   | Alcohol<br>(sp. gr. 0·825<br>at 60°)<br>per cent.<br>by measure. | Sp. gr.<br>of the<br>Wine. | Authority. |
|---|--|----------------------------|------------|---|--|----------------------------|------------|
| PORTUGUESE WINES.   |  |                            |            | SPANISH WINES—<br><i>continued.</i>                     |  |                            |            |
| Port .....  | 25·83  | ...                        | Brande     | Alba flora.....   | 17·26  | ...                        | Brande     |
| Ditto.....  | 24·89  | ...                        | Ditto      | Malaga (1666) .....                                     | 18·94  | ...                        | Ditto      |
| Ditto.....  | 23·71  | ...                        | Ditto      | Ditto.....  | 17·26  | ...                        | Ditto      |
| Ditto.....  | 23·39  | ...                        | Ditto      | WINES OF MADEIRA AND<br>THE CANARY ISLES.               |  |                            |            |
| Ditto.....  | 22·30  | ...                        | Ditto      | Madeira .....   | 24·42  | ...                        | Brande     |
| Ditto.....  | 21·40  | ...                        | Ditto      | Ditto.....  | 23·93  | ...                        | Ditto      |
| Ditto.....  | 19 00  | ...                        | Ditto      | Ditto.....  | 19·24  | ...                        | Ditto      |
| Ditto (Vinho de Ramo) ...   | 15·62  | ...                        | Prout      | Ditto (average) .....                                   | 22·27  | ...                        | Ditto      |
| Ditto (average) .....   | 22·96  | ...                        | Brande     | Sercial Madeira .....                                   | 21·40  | ...                        | Ditto      |
| Ditto (average) .....   | 20·64  | 0·9890                     | Prout      | Ditto.....  | 15·45  | ...                        | Christison |
| Ditto (weakest) .....   | 14·97  | ...                        | Christison | Madeira (long in cask<br>in the East Indies) } .....    | 16·90  | ...                        | Ditto      |
| Ditto (strongest).....  | 17·10  | ...                        | Ditto      | strongest.....  |  |                            |            |
| Ditto (mean of 7 samples) ..  | 16·20  | ...                        | Ditto      | Ditto ditto weakest                                     | 14·09  | ...                        | Ditto      |
| White Port .....  | 14·97  | ...                        | Ditto      | Ditto (West Indian) .....                               | 21·20  | 0·9908                     | Prout      |
| Colares.....  | 19·75  | ...                        | Brande     | Red Madeira .....                                       | 22·30  | ...                        | Brande     |
| Caravella .....   | 19·20  | ...                        | Ditto      | Ditto.....  | 18·40  | ...                        | Ditto      |
| Ditto.....  | 18·10  | ...                        | Ditto      | Ditto (average) .....                                   | 20·51  | ...                        | Ditto      |
| Ditto (average) .....   | 18·65  | ...                        | Ditto      | Malmsey .....   | 16·40  | ...                        | Ditto      |
| Lisbon .....  | 18·94  | ...                        | Ditto      | Ditto.....  | 12 86  | ...                        | Christison |
| Ditto (dry) .....   | 16·14  | ...                        | Christison | Teneriffe .....   | 19·79  | ...                        | Brande     |
| Bucellas .....  | 18·49  | ...                        | Brande     | FRENCH WINES.   |  |                            |            |
| Vidonia.....  | 19·25  | ...                        | Ditto      | Claret .....  | 17·11  | ...                        | Brande     |
| SPANISH WINES.  |  |                            |            | Ditto.....  | 16·32  | ...                        | Ditto      |
| Sherry .....  | 16·81  | ...                        | Brande     | Ditto.....  | 14·08  | ...                        | Ditto      |
| Ditto.....  | 19·83  | ...                        | Ditto      | Ditto.....  | 12·91  | ...                        | Ditto      |
| Ditto.....  | 18·79  | ...                        | Ditto      | Ditto (average) .....                                   | 15 10  | ...                        | Ditto      |
| Ditto.....  | 18·25  | ...                        | Ditto      | Ditto (first growth of 1811) ..                         | 7·72   | ...                        | Christison |
| Ditto.....  | 21·34  | 0·9752                     | Ditto      | Ditto (Chateau Latour, }<br>first growth of 1825) ... } | 7·78   | ...                        | Ditto      |
| Ditto (average) .....   | 19·17  | ...                        | Ditto      | Ditto (Rosan, second }<br>growth, 1825) .....           | 7·61   | ...                        | Ditto      |
| Ditto (very old .....   | 23 86  | ...                        | Prout      | Ditto (Vin Ordinaire).....                              | 8·99   | ...                        | Ditto      |
| Ditto (weakest) .....   | 13·98  | ...                        | Christison | Champagne (still) .....                                 | 13·80  | ...                        | Brande     |
| Ditto (strongest) .....   | 16·17  | ...                        | Ditto      | Ditto (sparkling) ..                                    | 12·80  | ...                        | Ditto      |
| Ditto (mean of 13 samples) ..   | 15·37  | ...                        | Ditto      | Ditto (red) .....                                       | 12·56  | ...                        | Ditto      |
| Ditto (mean of 9 samples }<br>very long kept in cask }<br>in the East Indies) ... } | 14·72  | ...                        | Ditto      |   |  |                            |            |
| Ditto Madre de Xeres ...  | 16·90  | ...                        | Ditto      |   |  |                            |            |
| Amontillado.....  | 12 63  | ...                        | Ditto      |   |  |                            |            |
| Tent .....  | 13·30  | ...                        | Brande     |   |  |                            |            |



Alcohol  
(sp. gr. 0·825  
at 60°)  
per cent.  
by measure.

Sp. gr.  
of the  
Wine.

Authority.

### FRENCH WINES— *continued.*

|                            |           |       |               |
|----------------------------|-----------|-------|---------------|
| Champagne (pink).....      | 11·30 ... | ...   | Brande        |
| Ditto (average).....       | 12·61 ... | ...   |               |
| Ditto.....                 | 12·20 ... | ...   | J. Fontenelle |
| Burgundy .....             | 16·60 ... | ...   | Brande        |
| Ditto.....                 | 15·22 ... | ...   | Ditto         |
| Ditto.....                 | 14·53 ... | ...   | Ditto         |
| Ditto.....                 | 11·95 ... | ...   | Ditto         |
| Ditto (average) .....      | 14·57 ... | ...   | Ditto         |
| Ditto (20 years in bottle) | 12·16 ... | ...   | Prout         |
| Hermitage (white) .....    | 17·43 ... | ...   | Brande        |
| Ditto (red) .....          | 12·32 ... | ...   | Ditto         |
| Côte Rôti .....            | 12·32 ... | ...   | Ditto         |
| Roussillon .....           | 19·06 ... | ...   | Ditto         |
| Ditto.....                 | 17·26 ... | ...   | Ditto         |
| Ditto (average) .....      | 18·13 ... | ...   | Ditto         |
| Sauterne .....             | 14·22 ... | ...   | Ditto         |
| Nice .....                 | 14·63 ... | ...   | Ditto         |
| Barsac .....               | 13·86 ... | ...   | Ditto         |
| Vin de Graves.....         | 13·94 ... | ...   | Ditto         |
| Ditto.....                 | 12·80 ... | ...   | Ditto         |
| Ditto (average) .....      | 12·08 ... | ...   | Ditto         |
| Grenache.....              | 21·24 ... | 1·053 | Prout         |
| Frontignan .....           | 12·79 ... | ...   | Brande        |
| Rivesalte .....            | 9·31 ...  | ...   | Christison    |
| Lunel .....                | 15·52 ... | ...   | Brande        |
| Ditto.....                 | 18·01 ... | ...   | J. Fontenelle |

### SICILIAN AND ITALIAN WINES.

|                            |           |        |         |
|----------------------------|-----------|--------|---------|
| Marsala .....              | 26·03 ... | ...    | Brande  |
| Ditto.....                 | 25·05 ... | ...    | Ditto   |
| Ditto (average) .....      | 25·09 ... | ...    | Ditto   |
| Ditto (21 years old).....  | 18·20 ... | ...    | Prout   |
| Lissa.....                 | 26·47 ... | ...    | Brande  |
| Ditto.....                 | 24·35 ... | ...    | Ditto   |
| Ditto (average) .....      | 25·41 ... | ...    | Ditto   |
| Ditto.....                 | 15·90 ... | 0·9913 | Prout   |
| Laehryma .....             | 19·70 ... | ...    | Brande  |
| Syracuse .....             | 15·28 ... | ...    | Ditto   |
| Ditto.....                 | 30·00 ... | 0·9911 | Prout   |
| Etna (red) .....           | 18·90 ... | ...    | Faraday |
| Ditto (white) .....        | 18·16 ... | ...    | Ditto   |
| Ditto (Sercial).....       | 19·00 ... | ...    | Ditto   |
| Ditto (white Falernian)... | 18·99 ... | ...    | Ditto   |
| Ditto (red Falernian)..... | 20·00 ... | ...    | Ditto   |
| Aleatico .....             | 16·20 ... | 1·020  | Prout   |

### GERMAN WINES.

|                           |           |        |            |
|---------------------------|-----------|--------|------------|
| Hochheimer .....          | 14·37 ... | ...    | Brande     |
| Ditto .....               | 13·00 ... | ...    | Ditto      |
| Ditto (old in cask) ...   | 8·88 ...  | ...    | Ditto      |
| Ditto (average) ...       | 12·08 ... | ...    | Ditto      |
| Johannisberger (1788) ... | 8·71 ...  | 0·9978 | Prout      |
| Rudesheimer (1811) ...    | 10·72 ... | 0·9937 | Ditto      |
| Ditto (1800) ...          | 12·22 ... | ...    | Ziz        |
| Ditto (superior) ...      | 8·40 ...  | ...    | Christison |
| Ditto (inferior) ...      | 6·90 ...  | ...    | Ditto      |
| Hambacher .....           | 7·35 ...  | ...    | Ditto      |
| Oestricher (1801) .....   | 8·46 ...  | 0·9960 | Ziz        |
| Ditto (1802) .....        | 10·50 ... | 0·9890 | Ditto      |
| Ditto (1804) .....        | 10·66 ... | 0·9920 | Ditto      |
| Zornheimer (1802) .....   | 10·11 ... | 0·9790 | Ditto      |
| Ditto (1803) .....        | 9·00 ...  | 0·9960 | Ditto      |

Alcohol  
(sp. gr. 0·825  
at 60°)  
per cent.  
by measure.

Sp. gr.  
of the  
Wine.

Authority.

### GERMAN WINES— *continued.*

|                          |           |        |       |
|--------------------------|-----------|--------|-------|
| Zornheimer (1804) .....  | 8·75 ...  | 1·031  | Ziz   |
| Bodenheimer (1802) ..... | 13·96 ... | 0·9890 | Ditto |
| Rhenish .....            | 7·58 ...  | 0·9997 | Prout |
| Ditto .....              | 7·36 ...  | 0·9992 | Ditto |
| Ditto .....              | 7·00 ...  | 0·9968 | Ditto |

### CAPE WINES.

|                          |           |       |        |
|--------------------------|-----------|-------|--------|
| Cape Madeira .....       | 22·94 ... | ...   | Brande |
| Ditto.....               | 20·50 ... | ...   | Ditto  |
| Ditto.....               | 18·11 ... | ...   | Ditto  |
| Ditto (average) .....    | 20·51 ... | ...   | Ditto  |
| Cape Muscat .....        | 18·25 ... | ...   | Ditto  |
| Constantia (white) ..... | 19·75 ... | ...   | Ditto  |
| Ditto (red) .....        | 18·92 ... | ...   | Ditto  |
| Ditto.....               | 14·50 ... | 1·081 | Prout. |

### HUNGARIAN WINE.

|             |          |     |        |
|-------------|----------|-----|--------|
| Tokay ..... | 9·88 ... | ... | Brande |
|-------------|----------|-----|--------|

### PERSIAN.

|               |           |        |            |
|---------------|-----------|--------|------------|
| Sheraaz ..... | 15·52 ... | ...    | Brande     |
| Ditto.....    | 12·95 ... | ...    | Christison |
| Ditto.....    | 19·80 ... | 0·9944 | Prout      |

### BRITISH WINES.

|                           |           |     |        |
|---------------------------|-----------|-----|--------|
| Grape wine .....          | 18·11 ... | ... | Brande |
| Raisin wine.....          | 26·40 ... | ... | Ditto  |
| Ditto.....                | 25·77 ... | ... | Ditto  |
| Ditto.....                | 23·20 ... | ... | Ditto  |
| Ditto (average) .....     | 25·12 ... | ... | Ditto  |
| Currant wine .....        | 20·55 ... | ... | Ditto  |
| Gooseberry wine.....      | 11·84 ... | ... | Ditto  |
| Orange wine (average) ... | 11·26 ... | ... | Ditto  |
| Elder wine .....          | 8·79 ...  | ... | Ditto  |
| Mead .....                | 7·32 ...  | ... | Ditto  |
| Cider.....                | 9·87 ...  | ... | Ditto  |
| Ditto.....                | 5·21 ...  | ... | Ditto  |
| Ditto (average) .....     | 7·54 ...  | ... | Ditto  |
| Perry (average) .....     | 7·26 ...  | ... | Ditto  |

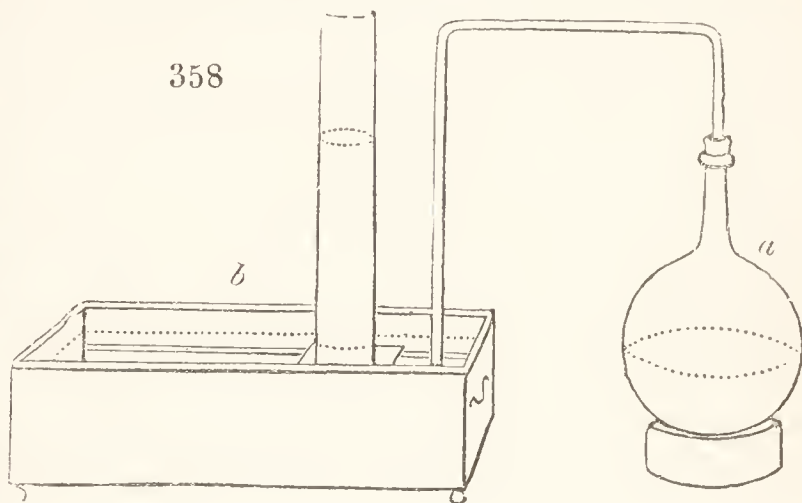
### MALT LIQUORS.

|                              |           |     |            |
|------------------------------|-----------|-----|------------|
| Ale, Burton .....            | 8·88 ...  | ... | Brande     |
| Ditto, Edinburgh .....       | 6·22 ...  | ... | Ditto      |
| Ditto, London (average)...   | 6·20 ...  | ... | Ditto      |
| Ditto, Dorchester .....      | 5·56 ...  | ... | Ditto      |
| Ditto (private brewery) ...  | 9·85 ...  | ... | Ditto      |
| Ditto ( ditto ) ...          | 10·84 ... | ... | Ditto      |
| Brown stout .....            | 6·80 ...  | ... | Ditto      |
| London porter (average)      | 4·20 ...  | ... | Ditto      |
| London small beer (average)  | 1·28 ...  | ... | Ditto      |
| Edinburgh ale (in cask)...   | 7·35 ...  | ... | Christison |
| Ditto (4 months in bottle)   | 5·36 ...  | ... | Ditto      |
| Ditto (2 years in bottle)... | 5·70 ...  | ... | Ditto      |

### SPIRITUOUS LIQUORS.

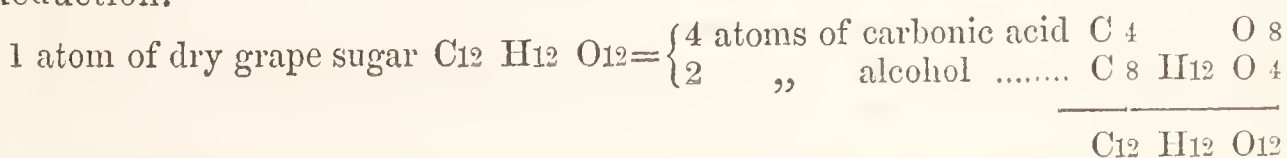
|                      |           |     |        |
|----------------------|-----------|-----|--------|
| Brandy.....          | 53·40 ... | ... | Brande |
| Rum .....            | 53·68 ... | ... | Ditto  |
| Gin .....            | 57·60 ... | ... | Ditto  |
| Scotch Whiskey ..... | 54·32 ... | ... | Ditto  |
| Irish Whiskey.....   | 53·90 ... | ... | Ditto  |

*Theory of Fermentation.* Sugar is resolved into *alcohol*,  $C_4 H_6 O_2$ , and *carbonic acid*,  $CO_2$ , by the process of *alcoholic* or *vinous fermentation*; this process, regarded under its simplest conditions, consists in adding a certain quantity of *yeast*, or other *ferment*, to an aqueous solution of *sugar*. Carbonic acid soon begins to be evolved, and the alcohol which is at the same time formed, remains combined with the water. The experiment may be most conveniently conducted upon a small scale in the annexed form of apparatus: the syrup and yeast are introduced into the bottle *a*, from which a bent tube issues, passing under the inverted jar placed in the water-trough *b*. It will now be found, that all that is requisite to induce fermentation, and the consequent production of alcohol from the above materials, is to subject them to a *due temperature*, say between  $70^\circ$  and  $80^\circ$ ; they



then soon begin to act upon each other, and the principal points to be noticed are, 1. that *carbonic acid* is evolved; 2. that the *sugar* gradually disappears; and, 3. that *alcohol* is gradually formed. It will be further observed that the contact of air (or oxygen) is unnecessary; it is indeed in many instances injurious.

As respects the *quantitative results* of this experiment, it has been ascertained by Dubrunfaut, and by Boullay and Dumas (*Chim. app. aux Arts*, vi. 314), that if we set out with *cane sugar*, it is, in the first instance, converted into *glucose*, or *grape sugar*, and that the *grape sugar* is then resolved into carbonic acid and alcohol. Now grape sugar, which in its ordinary hydrated or crystalline state is  $= C_{12} H_{14} O_{14}$  (see p. 1185) loses, when carefully dried at a little above  $212^\circ$ , 2 atoms of water, and becomes  $C_{12} H_{12} O_{12}$ ; and assuming such to be its composition, 1 atom of the anhydrous grape sugar would be resolved exactly into 4 atoms of carbonic acid and 2 atoms of alcohol; or, in other words, 180 parts of the dry grape sugar would yield 88 parts of carbonic acid and 92 of alcohol; and the results of experiment sanction this theoretical deduction.



We accordingly find that if we set out with *cane sugar*  $= C_{12} H_{11} O_{11}$ , it yields somewhat *more* than its weight of carbonic acid and alcohol, inasmuch as it in the first instance assimilates to itself an atom of water to form *grape sugar*. If on the other hand we commence with *common grape sugar*  $= C_{12} H_{14} O_{14}$ , it yields *less* than its weight of carbonic acid and alcohol, because it contains 2 atoms of water in excess; hence we have, on the one hand, 171 parts of *cane sugar* producing 180 parts of carbonic acid and alcohol; and on other 198 parts of *common grape sugar* produce the same results. It is also found that a very small quan-



tity of *ferment* is required to excite the fermentation of grape sugar or glucose, whereas cane sugar requires a much larger proportion.

In the production of beer and wine, and in the case of the fermentation of a solution of sugar, as just described, the results, as relate to the production of *alcohol*, are the same; the sugar is decomposed *in consequence of the presence of a ferment*. When *yeast* is used, its particles are seen to become covered with small bubbles of carbonic acid, which cause them to rise to the surface of the liquor; where they discharge it, and as they again sink they gradually acquire a fresh coating of bubbles, which they carry up as before; and in this way that motion of the whole mass of liquor is produced which is so characteristic of active fermentation, and which, provided a sufficiency of ferment be present, is maintained as long as any sugar remains to be decomposed. The process is also attended by a considerable elevation of temperature, and when complete, the liquor clears, the yeast falls to the bottom, the sugar has vanished, and is as it were replaced by alcohol. A trace of ammonia also at the same time makes its appearance.

These extraordinary changes can only be brought about by the action of *yeast*, or some analogous *ferment*; its *modus operandi* has been the subject of much experiment and discussion, and involves some very curious considerations.

It has been shown by Mitscherlich (*Poggend. Ann.*, lv. 224) that the actual contact of the particles of the yeast with the dissolved sugar is essential. He suspended a wide glass tube, the bottom of which was made of bibulous paper, in a jar of a solution of sugar, the tube being itself filled with the same solution. Some yeast was then put into the syrup contained in the tube, where it soon induced fermentation, and the alcohol there formed, passed through the pervious bottom, and, together with carbonic acid, diffused itself in the surrounding liquor; but the actual phenomena of fermentation, namely, the destruction of the sugar and the formation of alcohol and of carbonic acid, were limited to the syrup in the tube containing the ferment, and the sugar in the outer vessel remained unchanged. So also Quevenne found that yeast which had been deprived of all matter soluble in water, still retained its power of exciting fermentation. (*Journ. de Pharm.*, xxiv. and xxvii.) But it has also been shown by Mitscherlich, (*Ann. Ch. et Ph.*, 3ème Sér., vii. 15,) and by Quevenne, and more especially by Cagniard de Latour, (*Ann. Ch. et Ph.*, lxviii. 206,) and by Turpin, (*Mémoires de l'Institut*, xvii. 93, and *Bibliothèque Universelle*, Nov. 1838,) that the active part of yeast or barm is composed of minute vesicles, containing globules, and that these *germinate* in the saccharine liquor, and produce a microscopic plant, the *Torula Cerevisiæ* (Nat. ord. *Fungi*, subd. *Mucedines*). Desmazières describes this plant under the name of *Micoderma Cerevisiæ*. According to these authorities, the plant grows at the expense of the sugar, giving out carbonic acid, and leaving alcohol. According to Andral and Gavarret, (*Ann. Ch. et Ph.*, 3ème Sér., viii. 399,) there are two species of vegetable seeds contained in yeast, which may be separated by diluting it with water; in a few days globules fall to the bottom of the vessel, forming a grey pulverulent deposit which is extremely active in producing alcoholic fermentation when added to saccharine solutions; but at the same time a film forms upon the surface of the liquid, which

consists of germs (of *Penicillium glaucum*) having no power of exciting fermentation: these latter germs make their appearance in all acid albuminous liquids, and become *filamentous*, while the true producer of alcoholic fermentation always retains its distinct *globular* form. According to Mitscherlich, the active part of yeast which remains after it has been washed with water, consists of, carbon 47·0, hydrogen 6·6, oxygen 35·8, nitrogen 10·0, sulphur 0·6 *per cent.*; it also contains a trace of phosphorus, and of fixed bases. Of this yeast, from 2 to 3 parts are required for the decomposition of 100 parts of sugar; and if there be excess of sugar, it remains unchanged after the fermentation. That portion of the yeast which remains in the form of a deposit after fermentation is over, is inefficient as a ferment; it appears, when examined under the microscope, to consist of the ruptured cells, and is unsusceptible of vegetation; so that during the fermentation of sugar, a certain portion of the yeast-plant dies, and is decomposed, the living plant being required to sustain the fermentative process. If more yeast be present than is required for the decomposition of a certain quantity of sugar, the deposit which is in that case formed consists partly of broken and partly of entire cells, and the latter retain their power of inducing fermentation. (MITSCHERLICH. CAGNIARD DE LATOUR.) It would further appear that that portion of the yeast which has become inert as a ferment, has lost the greater part, if not the whole of its nitrogen; and certainly, one of the results of the changes which ensue during saccharine fermentation, appears to be the formation of ammonia, which, though so small in quantity as generally to elude observation, may, as already remarked, be easily detected amongst the gaseous products.

For the *formation of yeast or ferment*, the requisites appear to be the presence of sugar and of an azotized principle in aqueous solution, and the contact of air. A solution of pure sugar undergoes no change, but the addition to it of any proteiniferous compound, with the access of air, induces fungous vegetation, and with it fermentation. In all sweet fruits, grape sugar and some form of proteine are present, and their juices are accordingly susceptible of fermentation; although, as Gay-Lussac's experiments above cited have shown, they also require the presence of oxygen. Grape juice carefully preserved from the contact of air, as when expressed in an atmosphere of hydrogen, or of carbonic acid, may be kept for months without fermentative change; yet, upon the admission of a few bubbles of air, or of oxygen, it presently begins to ferment, and when the process has once commenced, it goes on. But it has been shown by Schwann, (*Poggend. Ann.*, xli. 184,) that a fermentable liquor, namely, one containing sugar and an azotized principle, undergoes no change when the air which has access to it has been previously passed through a red-hot tube; and Ure and Helmholtz have repeated the experiments with similar results; hence it has been assumed that the germs or seeds of the fungi are present in the atmosphere, and only await the requisite conditions and food for their vegetation, which they find in saccharine and other liquors; and that the vitality of these germs is destroyed by a certain elevation of temperature. Yet, in Gay-Lussac's experiments, a few bubbles of *pure oxygen gas* (in which, from the mode of its preparation, organic germs cannot be supposed to exist) induced fermentation; and he further states, that on decomposing a por-



tion of must excluded from air, by the voltaic current, fermentation ensued, apparently in consequence of the evolved oxygen: but Helmholtz could not obtain this result. (GAY-LUSSAC, *Ann. de Chimie*, LXXVI. 245. THENARD, *ibid.*, XLVI. 294. See also LÖWIG, *Chim. der Org. Verbind.*, i. 228, where this question is discussed in reference to *equivocal generation*.) According to Mitscherlich (*Lehrbuch*, 4th Ed.) *animalcules* are also concerned in the phenomena of fermentation; thus, if a little sugar be added to a liquor containing *infusoria*, the animalcules increase rapidly, and ferment is at the same time formed; on adding more sugar, the multiplication of the animalcules ceases, but there is an increase in the production of the ferment.

To obtain a ferment, in the first instance, a quantity of ground malt may be made into a thick paste by the addition of some concentrated wort, at a temperature of about  $70^{\circ}$  to  $75^{\circ}$ , so as to convert the starch into sugar; a little alcohol is then added, and after a few days, when the violence of the fermentation has subsided, a deposit of ferment is formed. Fownes prepares what he terms *artificial yeast*, as follows:—“A small handful of ordinary wheat flour was made into thick paste with cold water, covered with paper, and left seven days on the mantel-shelf of a room where a fire was kept all day, being occasionally stirred: at the end of that period three quarts of malt were mashed with about two gallons of water, the infusion boiled with the proper quantity of hops, and when sufficiently cooled, the ferment added. The results of the experiment were, a quantity of beer, not very strong, it is true, but quite free from any unpleasant taste, and at least a pint of thick barm, which proved perfectly good for making bread.

“It appears to me that this simple plan would enable distant residents in the country, and settlers in the colonies, to enjoy the luxury of good bread when a little malt could be got; a very easy home manufacture from grain of any kind: the hops might probably be omitted when the yeast alone was the object.” (*Mem. Chem. Soc.*, i. 101.)

**BRANDY. RUM. GIN. WHISKEY, &c.** These names are given to the spirituous products obtained by distilling fermented liquors; they are of various flavors and qualities, dependent upon the sources whence they are derived, but they all contain alcohol and water, together with certain substances giving them peculiar odors and flavors.

*Brandy* is the result of the distillation of *wine*, and its qualities vary with the kind of wine from which it is obtained, and the precaution with which it is distilled.

Brandy, as usually sold, is generally stated to be about 10 *per cent.* *under proof*; but when recently imported, it is often a little *over proof*, so that its strength probably diminishes by keeping it in cask; its average specific gravity is 0.94, and it contains about 53 *per cent.* of alcohol (sp. gr. 0.825 at  $60^{\circ}$ ), or 42 *per cent.* of absolute alcohol (sp. gr. 0.791 at  $60^{\circ}$ ). The flavor and fragranciness of brandy is derived from a portion of essential oil, and of an ethereal product, which pass over along with the alcohol and water in the process of distillation. The most esteemed brandies are those distilled in France, especially those of Armagnac and Cognac: they are obtained from *white wines*; not that these yield more alcohol than the red wines, but that the latter are frequently fermented



with the skins and stalks of the grape, whence they derive matters, some of which communicate an undesirable flavor to the distilled liquor; these are chiefly œnanthic ether, a peculiar greasy oil, and the substances known as amylic or grain-oil, and potato-oil; a single drop of the latter infects a very large quantity of brandy, and it is the absence of these which constitutes the excellence of the finest French brandies (*Eau de Vie*, d'Andaye, de Cognac, &c.). These oily products are mostly less volatile than alcohol, so that when the process of rectification is carefully performed, they remain, with the residuary water, in the still or retort; and as regards the rectification of spirit of wine derived from distillers' wash, and other fermented infusions of grain, many precautions are requisite both in conducting the distillation and in the management and construction of the stills, so as to produce what is technically known as *clean spirit*.

According to Ure (*Dictionary*, Art. *Brandy*), genuine French brandy evinces an acid reaction with litmus paper, owing to the presence of a minute portion of acetic acid; it also contains acetic ether, and when long kept in oak casks, a little astringent matter; he gives the following as a mode of converting rectified corn-spirit into factitious brandy:—"Dilute the pure alcohol to the proof pitch; add to every hundred pounds weight of it from half a pound to a pound of argol (crude tartar) dissolved in water, a little acetic ether, and French wine-vinegar, some bruised French plums, and flavor-stuff from Cognac; then distil the mixture with a gentle fire in an alembic furnished with an agitator. The spirit which passes over may be colored with burned sugar to the desired tint, and roughened in taste with a few drops of tincture of catechu, or of oak-bark." This may probably be taken as a specimen of the processes adopted in the manufacture of what are termed *British brandies*: it at all events furnishes, as Dr. Ure observes, a spirit free from the deleterious drugs so often used to disguise and increase the intoxicating powers of these liquors, and one as wholesome as alcohol in any shape can ever be.

*Rum* is a spirituous liquor distilled in the West and East Indies from a fermented mixture of molasses and water with the skimmings from the sugar-boilers, and the lees or spirit-wash of former distillations, called *dunder*. The average strength of rum is 53 to 54 *per cent.* of alcohol (sp. gr. 0.825 at 60°), or about 42 *per cent.* of absolute alcohol. The peculiar flavor of rum is ascribed to an oily product, formed probably in the process of fermentation; to this also its sudorific power may probably be in part referred: it is usually considered more heating than brandy, though somewhat inferior to it in alcoholic strength.

*Gin*, or *Geneva* (from *Genievre*, Juniper), is prepared from different kinds of corn-spirit: it was originally largely imported from Holland, and hence known as *Hollands*, or *Hollands-gin*. Its flavor is derived from juniper-berries, or from the essential oil of juniper, which contributes to its diuretic quality. *Calamus aromaticus*, or *sweet flag*, and other flavoring articles, are occasionally used in its manufacture. The great gin-distillers sell it to the trade at about 20 *per cent.* under proof, but the retailers afterwards dilute and generally sweeten it. Accum states that 120 gallons of gin, as obtained from the wholesale distiller, are *made up* with 14 gallons of water and 26 pounds of sugar; but as

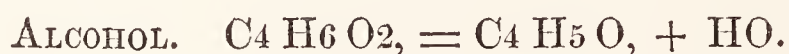


this operation renders the liquor milky, it is afterwards fined by dissolving in it a little alum and carbonate of potassa. (*On the Adulteration of Food, &c.* London, 1820.)

*Whiskey* (a term said to be derived from the Irish *usquebaugh*) is also a corn-spirit, and, when genuine, derives its characteristic flavor from the malt used in its manufacture having been dried over peat or turf fires; but this odor and flavor of burned turf, or *peat-reek*, is frequently given to raw corn-spirit by impregnating it with peat-smoke. The average strength of samples of genuine Scotch and Irish whiskey amounts to about 54 *per cent.* of alcohol (sp. gr. 0.825 at 60°).

*Arrack*, or *Rack*, is a spirituous liquor prepared in various parts of India from the fermented juice of the cocoa-nut, and also from fermented infusion of rice. It has a peculiar flavor, generally resembling that of a tan-pit, but in other respects closely approaches in its characters to rum. It is said that genuine arrack may be very well imitated by dissolving 10 grains of benzoic acid in a pint of rum.

There are many other alcoholic liquors, the preparation of which is peculiar to particular places. *Kirschwasser* is obtained in Switzerland, and in some parts of France, from bruised black cherries, fermented, and distilled. *Maraschino* is a similar liquor, prepared also from a peculiar kind of cherry growing in Dalmatia. *Noyau*, and several analogous *liqueurs*, are flavored with an essential oil containing more or less hydrocyanic acid, and often that derived from bitter almonds, the kernels of peaches, apricots, &c., or from the leaves of laurels. Some of these compounds come under the denomination of *tinctures*; such, for instance, as *Curaçoa*, which is prepared by digesting orange-berries (the immature fruit) and bitter orange peel with cloves and cinnamon in brandy: when this tincture is distilled, and afterwards sweetened, it constitutes *white Curaçoa*. These compounds are frequently called *Ratafias*, a term "derived, like the word *ratify*, from *ratum* and *fio*, to make firm, or confirm. By *ratafia*, therefore, was originally meant a liquid drank at the *ratification* of an agreement." (PEREIRA *On Food and Diet*, p. 165.)



By the careful distillation of any of the spirituous or fermented liquors above adverted to, the alcoholic portion may be separated from the less volatile matters, and thus obtained, it is known in commerce as *Rectified Spirit of Wine*. Its specific gravity is usually about 0.840 to 0.850, and it consists of alcohol combined with about from 17 to 20 *per cent.* of water; it also generally contains traces of oily matters, and of some other impurities. To obtain *pure*, or as it is frequently termed, *absolute alcohol*, spirit of wine is usually distilled off certain substances which have a high affinity for water, for although alcohol is more volatile than water, and rises in distillation at a lower temperature, pure alcohol can never be obtained by simply distilling rectified spirit, partly in consequence of the affinity which exists between aqueous and alcoholic vapor, and partly from the rising of a portion of watery vapor at the temperature required to distil over the alcohol; so that at whatever temperature aqueous alcohol is distilled, the product is never anhydrous. Various substances have been resorted to for the dehydration of alcohol,

such as carbonate of potassa (p. 593), anhydrous sulphate of soda (615), anhydrous sulphate of copper (834), and chloride of calcium (637); but nothing answers better than pure quicklime.

When common spirit of wine is used as the source of anhydrous alcohol, the first portions of water may be abstracted by adding to it dry carbonate of potassa till that salt ceases to be dissolved; the mixture is then frequently shaken, and when allowed to stand at rest soon separates into two portions, the uppermost being alcohol, and the lowermost an aqueous solution of the carbonate. The former is then drawn off and poured upon a quantity of powdered quicklime, amounting to about the weight of the alcohol, and previously introduced into a tubulated retort. This mixture may be left to digest for a day or two, and then slowly distilled in a water-bath, at a temperature of about  $200^{\circ}$ . (GAY-LUSSAC, *Ann. de Chim.*, LXXXvi. 175, and *Ann. Ch. et Ph.*, ii. 130. DRINK-WATER, *Mem. Chem. Soc.*, iii. 447.)

Some years ago Soemmering suggested a curious mode of depriving spirit of wine of water, consisting in putting it into a clean bladder, or into a glass vessel with a wide mouth, tied over with a bladder; it was found that the aqueous vapor penetrated the membrane in preference to the alcoholic vapor, so that by this kind of spontaneous evaporation, the strength of the alcohol remaining in the bladder or vessel is increased. Spirit of wine of the sp. gr. of 0.867 was thus easily reduced to 0.817. (*Quart. Journ.*, viii. 381, and xviii. 180.) But this, though an interesting illustration of *exosmose*, is not practically applicable to the production of anhydrous alcohol. The smugglers who bring spirits into Paris in bladders concealed about their persons, have long known, that although it lost bulk, it acquired strength; hence the preference given to the smuggled article. It has been also proposed to apply this principle to the ripening of wines. Soemmering tried it upon hock, (Asmanshäuser,) and found it greatly mellowed and improved. (*Denkschriften der Kön. Acad. der Wissensch. zu München*, 1811 to 1815. See also HENDERSON on *Wines*. Lond., 1824, p. 325.)

Professor Graham has ingeniously proposed to concentrate alcohol, as follows (*Edinb. Phil. Trans.*, 1828.) A shallow vessel is sprinkled over with coarsely-powdered quicklime, and a smaller one, containing spirit of wine, is placed just above it; both are covered with a proper bell-glass upon the plate of an air-pump, and the air exhausted till the alcohol begins to boil. Of the vapor which rises, the lime only absorbs the aqueous part, and as, under these circumstances, water cannot remain in alcohol, unless covered by an atmosphere of its own vapor, it continues in uninterrupted evaporation, whilst the escape of the alcohol is prevented by the pressure of its own unabsorbed vapor. If sulphuric acid be substituted as the absorbent instead of quicklime, it absorbs both vapors, and the whole of the spirit evaporates.

*Properties of Alcohol.* Alcohol is a limpid colorless liquid of an agreeable odor, and a strong pungent taste. From its action on the system it may be termed *poisonous*; when more or less dilute, it is *intoxicating*. The mode in which it kills animals, and the physiology of inebriation, have been studied by Orfila, (*Traité des Poisons*, ii. Part 2, p. 57, Ed. 1815,) and by Brodie, (*Phil. Trans.*, 1811, p. 179.) The specific gravity of *absolute alcohol* is 0.794 at  $60^{\circ}$  (0.7947 at  $59^{\circ}$ ,



RUDBERG; 0·7941, DRINKWATER.) The specific gravity assigned to the *alcohol* of the Pharmacopœia, is 0·820 at 60°. When spirit of wine is as far as possible dehydrated by simple distillation, its specific gravity is 0·825 at 60°. The *rectified spirit* of the Pharmacopœia is directed to have the sp. gr. 0·835. The real quantity of absolute alcohol contained in these and other commercial forms of alcohol and spirit of wine, will be seen by reference to the tables given further on. According to Dumas, the specific gravity of absolute alcohol at 59° being 0·7947; at 63° it is 0·79235; at 68°, 0·791; at 170°, 0·73869: these numbers have reference to water *at its maximum of density* as unity. According to Despretz, the specific heat of alcohol is 0·52. Alcohol has never been frozen. Faraday exposed it to a temperature of 166° below 0° (*Fahr.*); it thickened considerably, but did not congeal, (*Phil. Trans.*, 1845, p. 158.) According to Mitchell, (*Silliman's Journ.*,) alcohol of 0·798 becomes oily at - 130°, and at - 146° flows like melted wax; and alcohol of sp. gr. 0·820 entirely congeals in the bath of solid carbonic acid and ether. The solidification of alcohol, sp. gr. 0·798, as announced by Hutton, (*Nicholson's Journ.*, xxxiv. 166,) seems to have been an error. The boiling-point of alcohol of sp. gr. 0·7947 is 173° (Barom. 29·5.) When of sp. gr. 0·825 it boils at the temperature of 176° under the same pressure. According to Dalton, the boiling-point of alcohol of sp. gr. 0·800 is 173·5, and when raised by the addition of water to sp. gr. 0·900, its boiling-point is elevated to 182°. A table of the boiling-points of various mixtures of alcohol and water founded on Groening's experiments, is given in the *Annals of Philosophy*, N.S., v. 313. In the vacuum of an air-pump alcohol boils at common temperatures. The specific gravity of the *vapor of alcohol* (in reference to air as = 1·000) was experimentally found by Gay-Lussac to be 1·6133; its calculated specific gravity (upon the assumption that it consists of 1 volume of olefiant gas and 1 volume of aqueous vapor, condensed into 1 volume of alcohol vapor) is 1·6030. (GAY-LUSSAC, *Ann. Ch. et Ph.*, i. 218.) According to Berzelius and Dulong, the density of the vapor of absolute alcohol is 1·6004. (*Ann. Ch. et Ph.*, xv. 395.) The latent heat of the vapor of alcohol is to that of the vapor of water as 332 to 531. (DESPRETZ, *Ann. Ch. et Ph.*, xxiv. 329.) Dr. Ure has given the elastic force of the vapor of alcohol (of sp. gr. 0·813) at different temperatures in the following table. (*Phil. Trans.*, 1818, p. 359.)

| Temp. | Force of Vapor. | Temp. | Force of Vapor. | Temp. | Force of Vapor. | Temp. | Force of Vapor. |
|-------|-----------------|-------|-----------------|-------|-----------------|-------|-----------------|
| 32°   | 0·40            | 110°  | 6·00            | 180°  | 34·73           | 236°  | 103·60          |
| 40    | 0·56            | 115   | 7·10            | 182·3 | 36·40           | 238   | 109·90          |
| 45    | 0·70            | 120   | 8·10            | 185·3 | 39·90           | 240   | 111·24          |
| 50    | 0·86            | 125   | 9·25            | 190   | 43·20           | 244   | 118·20          |
| 55    | 1·00            | 130   | 10·60           | 193·3 | 46·60           | 247   | 122·10          |
| 60    | 1·23            | 135   | 12·15           | 196·3 | 50·10           | 248   | 126·10          |
| 65    | 1·49            | 140   | 13·90           | 200   | 53·00           | 249·7 | 131·40          |
| 70    | 1·76            | 145   | 15·95           | 206   | 60·10           | 250   | 132·30          |
| 75    | 2·10            | 150   | 18·00           | 210   | 65·00           | 252   | 138·60          |
| 80    | 2·45            | 155   | 20·30           | 214   | 69·30           | 254·3 | 143·70          |
| 85    | 2·93            | 160   | 22·60           | 216   | 72·20           | 258·6 | 151·60          |
| 90    | 3·40            | 165   | 25·40           | 220   | 78·50           | 260   | 155·20          |
| 95    | 3·90            | 170   | 28·30           | 225   | 87·50           | 262   | 162·40          |
| 100   | 4·50            | 173   | 30·00           | 230   | 94·10           | 264   | 166·10          |
| 105   | 5·20            | 178·3 | 33·50           | 232   | 97·10           |       |                 |

The expansibility of alcohol by heat is such that 1000 measures (sp. gr. 0·817) at 50°, become 1079 measures at 170°. At 110°, half-way between the extremes, the alcohol was at 1039, or half a division below the true mean. The more the alcohol is diluted with water, the greater is the disproportion between the two parts of the scale. When of the sp. gr. 0·967, corresponding to 75 *per cent.* of water, the rate of expansion through the first half between 50° and 170°, was to the second half, as 35 to 45. (DALTON. *Henry's Elements of Chemistry*, ii. 319, 9th Ed.) In the *Ann. de Chim. et Phys.* for January, 1837 (Lxiv., 1,) is an elaborate paper by Muncke, of Heidelberg, on the dilatation of absolute alcohol, and of carburet of sulphur, by heat, in which are some valuable facts respecting the maximum density of those liquids, and their applications to thermometric purposes. He is of opinion that absolute alcohol (sp. gr. 0·791) attains its maximum density at  $-89\cdot4^{\circ}$  (*Centigrade*), and presumes that it would concrete at  $-92$  of the same scale; but Mitchell and Faraday have experimentally shown that these conclusions are erroneous.

The following table, showing the contraction of alcohol in cooling down from its boiling-point, is given by Dumas, as founded upon Gay-Lussac's experiments:—

| Temp.  |      |       |         | Temp. |      |       |         |
|--------|------|-------|---------|-------|------|-------|---------|
| Cent.  |      | Fahr. | Volume. | Cent. |      | Fahr. | Volume. |
| 78·14° | .... | 173°  | 1000·0  | 38·4° | .... | 101°  | 954·4   |
| 73·4   | .... | 164   | 994·4   | 33·4  | .... | 92    | 948·9   |
| 68·4   | .... | 155   | 988·6   | 28·4  | .... | 83    | 943·6   |
| 63·4   | .... | 146   | 982·5   | 23·4  | .... | 73    | 938·6   |
| 58·4   | .... | 136   | 975·7   | 18·4  | .... | 65    | 934·0   |
| 53·4   | .... | 128   | 970·9   | 13·4  | .... | 56    | 929·3   |
| 48·4   | .... | 119   | 965·3   | 8·4   | .... | 47    | 924·5   |
| 43·4   | .... | 110   | 960·0   | 3·4   | .... | 39    | 919·9   |

Absolute alcohol has so strong an affinity for water as to absorb it from the atmosphere; it requires, therefore to be kept in well-stopped bottles, as, after exposure, it undergoes a sensible increase of specific gravity; it is even apt to absorb a small quantity of water during its distillation. It may be mixed, in all proportions, with water, and in this case heat is evolved, and diminution of bulk (or increase of specific gravity) ensues. When alcohol and snow are mixed, there is, on the other hand, a diminution of temperature. The diminution of bulk which ensues on mixing alcohol with water, may be shown as follows —

The annexed woodcut represents a tube with two bulbs, communicating with each other, the upper one being supplied with a well-ground glass stopper. Fill the tube and lower bulb with *water*, pour *alcohol* slowly into the upper bulb, and when full, put in the stopper. The vessel will now be completely filled, the alcohol lying upon the water; if it be inverted, the alcohol and water will slowly mix, and the condensation that ensues will be indicated by the empty space in the tube; at the same time a considerable rise of temperature takes place in consequence of the diminished specific heat of the mixture.





Thus equal measures of alcohol (sp. gr. 0·825) and water, each at 50°, afford, when suddenly mixed, a temperature of 70°; and equal measures of *proof spirit* and water, each at 50°, give, under similar circumstances, a mixture of the temperature of 60°.

On thus mixing alcohol and water, the contraction increases till the mixture consists of 100 parts of alcohol and 116·23 of water. According to Rudberg, 100 volumes of this mixture, at 59°, contain 53·739 volumes of anhydrous alcohol, and 49·836 of water; the condensation, therefore, amounts to 3·575. The specific gravity is 0·927 at 59°. Departing from this point, the contraction produced by fresh additions of water becomes more and more feeble, and terminates in apparent dilatation; thus Tillaye found, that when equal volumes of dilute alcohol, specific gravity 0·954, and water, were mixed, the specific gravity became 0·9768; whereas, if there had been no expansion, the density would have been 0·9772. The following table, calculated by Rudberg, from the experimental results of Gay-Lussac and Tralles, further illustrates this subject. (*Ann. Ch. et Ph.*, xLviii. 33.)

| Volume of Alcohol<br>per cent. | Contraction, in hun-<br>dredths of the volume,<br>of the mixture, | Volume of Alcohol<br>per cent. | Contraction, in hun-<br>dredths of the volume,<br>of the mixture. |
|--------------------------------|---|--------------------------------|---|
| 100                            | 0·  | 50                             | 3·745   |
| 95                             | 1·18  | 45                             | 3·64  |
| 90                             | 1·94  | 40                             | 3·44  |
| 85                             | 2·47  | 35                             | 3·14  |
| 80                             | 2·87  | 30                             | 2·72  |
| 75                             | 3·19  | 25                             | 2·24  |
| 70                             | 3·44  | 20                             | 1·72  |
| 65                             | 3·615   | 15                             | 1·20  |
| 60                             | 3·73  | 10                             | 0·72  |
| 55                             | 3·77  | 5                              | 0·31  |

In reference to this table, Dumas remarks, that the maximum of contraction indicates 55 *per cent.* of alcohol, but that Rudberg's experiments place it at 54 *per cent.*, which is equivalent to 23 parts by weight of alcohol, and 27 of water; or assuming the atomic weight of alcohol as = 46, to 1 atom of alcohol, and 6 atoms of water, or 46 + 54.

The absolute amount of the contraction varies with the temperature; according to Tralles, at 39° it amounts to 3·97; at 52° to 3·77; at 64° to 3·60; and at 100° to 3·31. (See also GILPIN'S *Tables*.)

The *strength* of such spirituous liquors as consist of water and alcohol, is ascertained by their *specific gravity*, and for the purpose of levying duties upon them, this is determined by the *hydrometer*; but the only correct mode of ascertaining the specific gravity of liquids, is by weighing them in a delicate balance, against an equal volume of pure water, of a similar temperature\*.

\* There are other methods of judging of the strength of spirituous liquors, which, though useful, are not accurate, such as the taste, the size and appearance of the bubbles when shaken, the sinking or floating of olive oil in it, and the appearances that it exhibits when burned; if it burns away perfectly to dryness, and inflames gun-powder, or a piece of cotton immersed in it, it is considered as *alcohol*. The different spirituous liquors leave variable proportions of water, when thus burned in a graduated vessel. But it must be recollected that in rum, brandy, and several other spirits, the specific gravity is often interfered with by extractive, coloring, and saccharine substances, often *fraudulently* added with a view to increase the specific gravity, and therefore to diminish their apparent strength. In examining these

The facilities, however, in using the *hydrometer*, are such as to render it best fitted for the practical purposes of the Excise, and, consequently, a Committee of the Royal Society recommended to the Government a form of the instrument, which they considered best adapted to the purpose, accompanied by proper tables; the following extract from their *report* will explain the most important parts of this inquiry, as relating to the composition and density of PROOF SPIRIT, which is defined by Act of Parliament (58 George III. c. 28), to be such “as shall, at the temperature of 51 degrees by Fahrenheit’s thermometer, weigh exactly twelve-thirteenth parts of an equal measure of distilled water.” The temperature of the distilled water is not specified, but there can be no doubt that it also is referred to as at 51°\*.

“With regard to the substance, *alcohol*, upon which the excise duty is to be levied, there appears to be no reason, either philosophical or practical, why it should be considered as *absolute*. A definite mixture of alcohol and water is as invariable in its value as absolute alcohol can be. It is also invariable in its nature; and can be *more readily*, and with equal accuracy, identified by that only quality or condition to which recourse can be had in practice, namely, specific gravity. A *diluted alcohol* is, therefore, that which is recommended by us as the only excisable substance; and as, on the one hand, it will make no difference in the identification, and on the other, will be a great commercial advantage, it is further recommended that the standard be very nearly that of the present *proof spirit*.

“The proposition of your Committee is, that *standard spirit* be that which, consisting of alcohol and water alone, shall have a specific gravity of 0·92 at the temperature of 62° Fahr., water being unity at that same temperature; or, in other words, that it shall at 62° weigh  $\frac{92}{100}$ ths, or  $\frac{23}{25}$ ths of an equal bulk of water at the same temperature. The temperature of 62° Fahr. is recommended as the standard, because it is that at which water was taken in the late national survey and adjustment of weights and measures. The specific gravity of 0·92 is taken rather than 0·918633 (the specific gravity of present *proof spirit* at 62°), because the fraction expressing its relation to water is much more simple, and

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liquors, they should be *distilled* in the manner described above in reference to wine, and the specific gravity of the *distilled portion* will then give an indication of the proportion of alcohol, that may be relied on. In respect, however, to the *excise*, *distillation* is inconvenient, and is, therefore, only resorted to, in extreme, or suspicious cases.

\* Hitherto the term *proof spirit* has been but indefinitely employed. Dr. Thomson, quoting the Act of Parliament of 1762, states, that at the temperature of 60°, the specific gravity of proof spirit should be 0·916; and he also observes that *proof spirit* usually means a mixture of equal bulks of alcohol and water; but the specific gravity of such a mixture will, of course, depend upon that of the *standard*

*alcohol*, which is not specified. It appears from GILPIN’S *Tables*, that spirit of the specific gravity ·916, at 60°, consists, *by weight*, of 100 parts of alcohol, specific gravity ·825 at 60°, and 75 of water; and, *by measure*, of 100 parts of the same alcohol, and 61·87 of water. From the *Tables* of LOWITZ, quoted by Dr. Thomson, from *Crell’s Annals* (1796, i. 202), equal weights of alcohol, specific gravity ·796 at 60° (and which may be regarded as *pure alcohol*), and water, have a specific gravity of ·917, which is very near legal proof, and which, according to GILPIN’S *Tables*, contains 62·8 parts per cent. of his alcohol, *by measure*. The *proof spirit* of the *Pharmacopœia* (*spiritus tenuior*) is directed to be of the specific gravity ·930.



will facilitate the construction of the tables and the verification of the instruments proposed to be used.

“This definition of *standard spirit* appears to your Committee to be very simple, and yet as exact as it can be, or as any *other* standard spirit can be. This standard is rather weaker than the old *proof spirit*, in the proportion of nearly 1·1 gallon of the present *proof spirit*, *per cent.* But this disadvantage your Committee consider as trifling compared with the great convenience which will result if the specific gravity of 0·92 be taken rather than 0·918633.

“It may be interesting hereafter to ascertain what proportion of *absolute alcohol* enters into the composition of the recommended standard spirit, should the latter be adopted by the Government; but the point possesses not the slightest practical importance in relation to the present question. The proposed standard is in fact more definite, more sure, and more ascertainable than that of the alcohol which it must contain. Philosophers are not yet agreed upon the density of *absolute alcohol*, and the differences of specific gravity assigned to it, vary from ·7910 to ·7980. But assuming the truth to be somewhere within these extremes, the proposed standard would contain nearly one-half by weight of absolute alcohol. (·7947 at 59°, BERZELIUS; ·7960 at 60°, TURNER, from *Saussure*? ·7910 at 68°, BRANDE; ·7980, CHAUSSIER; ·79235 at 64°, GAY-LUSSAC.)

“In any mixture of alcohol and water, the *specific gravity* appears to be the only quality or condition to which recourse can be had for the practical purposes of the Excise, in order to indicate the proportion of standard spirit present. Your Committee are of opinion that the *hydrometer* is the instrument best fitted in the hands of the excise officer to indicate that specific gravity; and they think it ought to be so graduated as to give the indication of strength, not upon an arbitrary scale, but in terms of specific gravity at a fixed temperature, which, in the present case, should be 62°, or that of the standard spirit. The graduation in terms of specific gravity will not only supply a very minute yet sensible scale for the purpose of ascertaining smaller differences in the density than is done by the present scale, but will also afford an easy means of verifying the instruments when required.”

In the *Philosophical Transactions* for 1794, Mr. Gilpin has given a copious and valuable series of tables of the specific gravity of mixtures of alcohol and water, and of the condensation that ensues, with several other particulars. These Tables are extremely useful, as enabling us to ascertain, without difficulty, the relative quantity of alcohol contained in any mixture of known specific gravity. The original tables are very voluminous, and have been variously abridged: but as they are published separately, they should be in the hands of all persons engaged in these inquiries\*. As far as the experimental chemist is concerned, the following table, by Löwitz, will probably be found sufficient. It shows the quan-

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\* Many other tables besides those which I have here inserted or referred to, have been constructed, and some of them are extremely valuable: I would especially refer the reader to Gay-Lussac's Essay on Alco- | holometry, and to the tables which accompany it, and also to the tables published by Tralles, abstracts of both of which will be found in *Ure's Dictionary*, Art. *Alcohol*.

tity of *absolute alcohol* (specific gravity  $\cdot 7960$  at  $60^{\circ}$ ) contained in diluted alcohol of different specific gravities\*.

| 100 parts. |      | Sp. Gravity.    |                 | 100 parts. |      | Sp. Gravity.    |                 | 100 parts. |      | Sp. Gravity.    |                 |
|------------|------|-----------------|-----------------|------------|------|-----------------|-----------------|------------|------|-----------------|-----------------|
| Ale.       | Wat. | At $68^{\circ}$ | At $60^{\circ}$ | Ale.       | Wat. | At $68^{\circ}$ | At $60^{\circ}$ | Ale.       | Wat. | At $68^{\circ}$ | At $60^{\circ}$ |
| 100        | 0    | 0.791           | 0.796           | 66         | 34   | 0.877           | 0.881           | 32         | 68   | 0.952           | 0.955           |
| 99         | 1    | 0.794           | 0.798           | 65         | 35   | 0.880           | 0.883           | 31         | 69   | 0.954           | 0.957           |
| 98         | 2    | 0.797           | 0.801           | 64         | 36   | 0.882           | 0.886           | 30         | 70   | 0.956           | 0.958           |
| 97         | 3    | 0.800           | 0.804           | 63         | 37   | 0.885           | 0.889           | 29         | 71   | 0.957           | 0.960           |
| 96         | 4    | 0.803           | 0.807           | 62         | 38   | 0.887           | 0.891           | 28         | 72   | 0.959           | 0.962           |
| 95         | 5    | 0.805           | 0.809           | 61         | 39   | 0.889           | 0.893           | 27         | 73   | 0.961           | 0.963           |
| 94         | 6    | 0.808           | 0.812           | 60         | 40   | 0.892           | 0.896           | 26         | 74   | 0.963           | 0.965           |
| 93         | 7    | 0.811           | 0.815           | 59         | 41   | 0.894           | 0.898           | 25         | 75   | 0.965           | 0.967           |
| 92         | 8    | 0.813           | 0.817           | 58         | 42   | 0.896           | 0.900           | 24         | 76   | 0.966           | 0.968           |
| 91         | 9    | 0.816           | 0.820           | 57         | 43   | 0.899           | 0.902           | 23         | 77   | 0.968           | 0.970           |
| 90         | 10   | 0.818           | 0.822           | 56         | 44   | 0.901           | 0.904           | 22         | 78   | 0.970           | 0.972           |
| 89         | 11   | 0.821           | 0.825           | 55         | 45   | 0.903           | 0.906           | 21         | 79   | 0.971           | 0.973           |
| 88         | 12   | 0.823           | 0.827           | 54         | 46   | 0.905           | 0.908           | 20         | 80   | 0.973           | 0.974           |
| 87         | 13   | 0.826           | 0.830           | 53         | 47   | 0.907           | 0.910           | 19         | 81   | 0.974           | 0.975           |
| 86         | 14   | 0.828           | 0.832           | 52         | 48   | 0.909           | 0.912           | 18         | 82   | 0.976           | 0.977           |
| 85         | 15   | 0.831           | 0.835           | 51         | 49   | 0.912           | 0.915           | 17         | 83   | 0.977           | 0.978           |
| 84         | 16   | 0.834           | 0.838           | 50         | 50   | 0.914           | 0.917           | 16         | 84   | 0.978           | 0.979           |
| 83         | 17   | 0.836           | 0.840           | 49         | 51   | 0.917           | 0.920           | 15         | 85   | 0.980           | 0.981           |
| 82         | 18   | 0.839           | 0.843           | 48         | 52   | 0.919           | 0.922           | 14         | 86   | 0.981           | 0.982           |
| 81         | 19   | 0.842           | 0.846           | 47         | 53   | 0.921           | 0.924           | 13         | 87   | 0.983           | 0.984           |
| 80         | 20   | 0.844           | 0.848           | 46         | 54   | 0.923           | 0.926           | 12         | 88   | 0.985           | 0.986           |
| 79         | 21   | 0.847           | 0.851           | 45         | 55   | 0.925           | 0.928           | 11         | 89   | 0.986           | 0.987           |
| 78         | 22   | 0.849           | 0.853           | 44         | 56   | 0.927           | 0.930           | 10         | 90   | 0.987           | 0.988           |
| 77         | 23   | 0.851           | 0.855           | 43         | 57   | 0.930           | 0.933           | 9          | 91   | 0.988           | 0.989           |
| 76         | 24   | 0.853           | 0.857           | 42         | 58   | 0.932           | 0.935           | 8          | 92   | 0.989           | 0.990           |
| 75         | 25   | 0.856           | 0.860           | 41         | 59   | 0.934           | 0.937           | 7          | 93   | 0.991           | 0.991           |
| 74         | 26   | 0.859           | 0.863           | 40         | 60   | 0.936           | 0.939           | 6          | 94   | 0.992           | 0.992           |
| 73         | 27   | 0.861           | 0.865           | 39         | 61   | 0.938           | 0.941           | 5          | 95   | 0.994           |                 |
| 72         | 28   | 0.863           | 0.867           | 38         | 62   | 0.940           | 0.943           | 4          | 96   | 0.995           |                 |
| 71         | 29   | 0.866           | 0.870           | 37         | 63   | 0.942           | 0.945           | 3          | 97   | 0.997           |                 |
| 70         | 30   | 0.868           | 0.872           | 36         | 64   | 0.944           | 0.947           | 2          | 98   | 0.998           |                 |
| 69         | 31   | 0.870           | 0.874           | 35         | 65   | 0.946           | 0.949           | 1          | 99   | 0.999           |                 |
| 68         | 32   | 0.872           | 0.875           | 34         | 66   | 0.948           | 0.951           | 0          | 100  | 1.000           |                 |
| 67         | 33   | 0.875           | 0.879           | 33         | 67   | 0.950           | 0.953           |            |      |                 |                 |

\* French authors are still in the inconvenient habit of referring to *Baumé's hydrometer* in speaking of the specific gravities of liquids, both lighter and heavier than water: the following tables show the real specific gravities at the temperature of  $55^{\circ}$  *Fahr.*, corresponding with the *degrees* of Baumé's instrument.

| FOR LIQUIDS LIGHTER THAN WATER. |         |      |         | FOR LIQUIDS HEAVIER THAN WATER. |         |      |         |
|---------------------------------|---------|------|---------|---------------------------------|---------|------|---------|
| Deg.                            | Sp. Gr. | Deg. | Sp. Gr. | Deg.                            | Sp. Gr. | Deg. | Sp. Gr. |
| 10                              | = 1.000 | 21   | = .922  | 32                              | = .856  | 0    | = 1.000 |
| 11                              | .990    | 22   | .915    | 33                              | .852    | 27   | = 1.230 |
| 12                              | .985    | 23   | .909    | 34                              | .847    | 30   | 1.261   |
| 13                              | .977    | 24   | .903    | 35                              | .842    | 33   | 1.295   |
| 14                              | .970    | 25   | .897    | 36                              | .837    | 36   | 1.333   |
| 15                              | .963    | 26   | .892    | 37                              | .832    | 39   | 1.373   |
| 16                              | .955    | 27   | .886    | 38                              | .827    | 42   | 1.414   |
| 17                              | .949    | 28   | .880    | 39                              | .822    | 45   | 1.455   |
| 18                              | .942    | 29   | .874    | 40                              | .817    | 48   | 1.500   |
| 19                              | .935    | 30   | .867    |                                 |         | 51   | 1.547   |
| 20                              | .928    | 41   | .861    |                                 |         |      |         |



According to Drinkwater, Löwitz's table is not accurate in reference to the more dilute alcoholic mixtures ; he has therefore constructed the following table showing the specific gravity and composition of mixtures of alcohol and water, containing less than 10 *per cent.* of absolute alcohol. (*Mem. Chem. Soc.*, iii. 454.)

TABLE of the quantity of absolute alcohol (sp. gr. 0·79381 at 60°) by weight contained in mixtures of alcohol and water of the following specific gravities :—

| Specific gravity at 60° F. | Alcohol, per cent. by weight. | Specific gravity at 60° F. | Alcohol, per cent. by weight. | Specific gravity at 60° F. | Alcohol, per cent. by weight. | Specific gravity at 60° F. | Alcohol, per cent. by weight. | Specific gravity at 60° F. | Alcohol, per cent. by weight. |
|----------------------------|-------------------------------|----------------------------|-------------------------------|----------------------------|-------------------------------|----------------------------|-------------------------------|----------------------------|-------------------------------|
| 1·0000                     | 0·00                          | ·9967                      | 1·78                          | ·9934                      | 3·67                          | ·9901                      | 5·70                          | ·9869                      | 7·85                          |
| ·9999                      | 0·05                          | ·9966                      | 1·83                          | ·9933                      | 3·73                          | ·9900                      | 5·77                          | ·9868                      | 7·92                          |
| ·9998                      | 0·11                          | ·9965                      | 1·89                          | ·9932                      | 3·78                          | ·9899                      | 5·83                          | ·9867                      | 7·99                          |
| ·9997                      | 0·16                          | ·9964                      | 1·94                          | ·9931                      | 3·84                          | ·9898                      | 5·89                          | ·9866                      | 8·06                          |
| ·9996                      | 0·21                          | ·9963                      | 1·99                          | ·9930                      | 3·90                          | ·9897                      | 5·96                          | ·9865                      | 8·13                          |
| ·9995                      | 0·26                          | ·9962                      | 2·05                          | ·9929                      | 3·96                          | ·9896                      | 6·02                          | ·9864                      | 8·20                          |
| ·9994                      | 0·32                          | ·9961                      | 2·11                          | ·9928                      | 4·02                          | ·9895                      | 6·09                          | ·9863                      | 8·27                          |
| ·9993                      | 0·37                          | ·9960                      | 2·17                          | ·9927                      | 4·08                          | ·9894                      | 6·15                          | ·9862                      | 8·34                          |
| ·9992                      | 0·42                          | ·9959                      | 2·22                          | ·9926                      | 4·14                          | ·9893                      | 6·22                          | ·9861                      | 8·41                          |
| ·9991                      | 0·47                          | ·9958                      | 2·28                          | ·9925                      | 4·20                          | ·9892                      | 6·29                          | ·9860                      | 8·48                          |
| ·9990                      | 0·53                          | ·9957                      | 2·34                          | ·9924                      | 4·27                          | ·9891                      | 6·35                          | ·9859                      | 8·55                          |
| ·9989                      | 0·58                          | ·9956                      | 2·39                          | ·9923                      | 4·33                          | ·9890                      | 6·42                          | ·9858                      | 8·62                          |
| ·9988                      | 0·64                          | ·9955                      | 2·45                          | ·9922                      | 4·39                          | ·9889                      | 6·49                          | ·9857                      | 8·70                          |
| ·9987                      | 0·69                          | ·9954                      | 2·51                          | ·9921                      | 4·45                          | ·9888                      | 6·55                          | ·9856                      | 8·77                          |
| ·9986                      | 0·74                          | ·9953                      | 2·57                          | ·9920                      | 4·51                          | ·9877                      | 6·62                          | ·9855                      | 8·84                          |
| ·9985                      | 0·80                          | ·9952                      | 2·62                          | ·9919                      | 4·57                          | ·9886                      | 6·69                          | ·9854                      | 8·91                          |
| ·9984                      | 0·85                          | ·9951                      | 2·68                          | ·9918                      | 4·64                          | ·9885                      | 6·75                          | ·9853                      | 8·96                          |
| ·9983                      | 0·91                          | ·9950                      | 2·74                          | ·9917                      | 4·70                          | ·9884                      | 6·82                          | ·9852                      | 9·05                          |
| ·9982                      | 0·96                          | ·9949                      | 2·79                          | ·9916                      | 4·76                          | ·9883                      | 6·89                          | ·9851                      | 9·12                          |
| ·9981                      | 1·02                          | ·9948                      | 2·85                          | ·9915                      | 4·82                          | ·9882                      | 6·95                          | ·9850                      | 9·20                          |
| ·9980                      | 1·07                          | ·9947                      | 2·91                          | ·9914                      | 4·88                          | ·9881                      | 7·02                          | ·9849                      | 9·27                          |
| ·9979                      | 1·12                          | ·9946                      | 2·97                          | ·9913                      | 4·94                          | ·9880                      | 7·09                          | ·9848                      | 9·34                          |
| ·9978                      | 1·18                          | ·9945                      | 3·02                          | ·9912                      | 5·01                          | ·9879                      | 7·16                          | ·9847                      | 9·41                          |
| ·9977                      | 1·23                          | ·9944                      | 3·08                          | ·9911                      | 5·07                          | ·9878                      | 7·23                          | ·9846                      | 9·49                          |
| ·9976                      | 1·29                          | ·9943                      | 3·14                          | ·9910                      | 5·13                          | ·9877                      | 7·30                          | ·9845                      | 9·56                          |
| ·9975                      | 1·34                          | ·9942                      | 3·20                          | ·9909                      | 5·20                          | ·9876                      | 7·37                          | ·9844                      | 9·63                          |
| ·9974                      | 1·40                          | ·9941                      | 3·26                          | ·9908                      | 5·26                          | ·9875                      | 7·43                          | ·9843                      | 9·70                          |
| ·9973                      | 1·45                          | ·9940                      | 3·32                          | ·9907                      | 5·32                          | ·9874                      | 7·50                          | ·9842                      | 9·78                          |
| ·9972                      | 1·51                          | ·9939                      | 3·37                          | ·9906                      | 5·39                          | ·9873                      | 7·57                          | ·9841                      | 9·85                          |
| ·9971                      | 1·56                          | ·9938                      | 3·43                          | ·9905                      | 5·45                          | ·9872                      | 7·64                          | ·9840                      | 9·92                          |
| ·9970                      | 1·61                          | ·9937                      | 3·49                          | ·9904                      | 5·51                          | ·9871                      | 7·71                          | ·9839                      | 9·99                          |
| ·9969                      | 1·67                          | ·9936                      | 3·55                          | ·9903                      | 5·58                          | ·9870                      | 7·78                          | ·9838                      | 10·07                         |
| ·9968                      | 1·73                          | ·9935                      | 3·61                          | ·9902                      | 5·64                          |                            |                               |                            |                               |

Drinkwater gives the following table showing the results of his experiments upon the composition of *proof spirit*.

| Alcohol and water.  |                                | Specific gravity at 60° F. | Bulk of mixture of 100 measures of alcohol + 81·82 water. | Strength per cent. above proof of absolute alcohol. |
|---|--------------------------------|----------------------------|---|---|
| By weight.  | By measure.                    |                            |   |   |
| Alcohol. Water.<br>100 + 103·09<br>or in 100<br>49·24 + 50·76 | Alcohol. Water.<br>100 + 81·82 | ·91984                     | 175·25  | 75·25   |

Dr. Steel, partly from experiment, and partly from calculation, had also previously arrived at almost the same conclusion respecting the composition of proof-spirit, fixing it nearly at 49·2 alcohol, and 50·8 water. (*Records of General Science*, i. 222.)

The following is Fownes' table of the specific gravities of mixtures of alcohol and water. Though less extended than the preceding tables, it places the results in a form which is sometimes more convenient for practical reference. (*Phil. Trans.*, 1847. See also his *Manual of Elementary Chemistry*, 2nd Edit., p. 583.)

| Sp. Gr. at 60°. | Per centage<br>of real<br>Alcohol. | Sp. Gr. at 60°. | Per centage<br>of real<br>Alcohol. | Sp. Gr. at 60°. | Per centage<br>of real<br>Alcohol. |
|-----------------|------------------------------------|-----------------|------------------------------------|-----------------|------------------------------------|
| ·9991           | 0·5                                | ·9511           | 34                                 | ·8769           | 68                                 |
| ·9981           | 1                                  | ·9490           | 35                                 | ·8745           | 69                                 |
| ·9965           | 2                                  | ·9470           | 36                                 | ·8721           | 70                                 |
| ·9947           | 3                                  | ·9452           | 37                                 | ·8696           | 71                                 |
| ·9930           | 4                                  | ·9434           | 38                                 | ·8672           | 72                                 |
| ·9914           | 5                                  | ·9416           | 39                                 | ·8649           | 73                                 |
| ·9898           | 6                                  | ·9396           | 40                                 | ·8625           | 74                                 |
| ·9884           | 7                                  | ·9376           | 41                                 | ·8603           | 75                                 |
| ·9869           | 8                                  | ·9356           | 42                                 | ·8581           | 76                                 |
| ·9855           | 9                                  | ·9335           | 43                                 | ·8557           | 77                                 |
| ·9841           | 10                                 | ·9314           | 44                                 | ·8533           | 78                                 |
| ·9828           | 11                                 | ·9292           | 45                                 | ·8508           | 79                                 |
| ·9815           | 12                                 | ·9270           | 46                                 | ·8483           | 80                                 |
| ·9802           | 13                                 | ·9249           | 47                                 | ·8459           | 81                                 |
| ·9789           | 14                                 | ·9228           | 48                                 | ·8434           | 82                                 |
| ·9778           | 15                                 | ·9206           | 49                                 | ·8408           | 83                                 |
| ·9766           | 16                                 | ·9184           | 50                                 | ·8382           | 84                                 |
| ·9753           | 17                                 | ·9160           | 51                                 | ·8357           | 85                                 |
| ·9741           | 18                                 | ·9135           | 52                                 | ·8331           | 86                                 |
| ·9728           | 19                                 | ·9113           | 53                                 | ·8305           | 87                                 |
| ·9716           | 20                                 | ·9090           | 54                                 | ·8279           | 88                                 |
| ·9704           | 21                                 | ·9069           | 55                                 | ·8254           | 89                                 |
| ·9691           | 22                                 | ·9047           | 56                                 | ·8228           | 90                                 |
| ·9678           | 23                                 | ·9025           | 57                                 | ·8199           | 91                                 |
| ·9665           | 24                                 | ·9001           | 58                                 | ·8172           | 92                                 |
| ·9652           | 25                                 | ·8979           | 59                                 | ·8145           | 93                                 |
| ·9638           | 26                                 | ·8956           | 60                                 | ·8118           | 94                                 |
| ·9623           | 27                                 | ·8932           | 61                                 | ·8089           | 95                                 |
| ·9609           | 28                                 | ·8908           | 62                                 | ·8061           | 96                                 |
| ·9593           | 29                                 | ·8886           | 63                                 | ·8031           | 97                                 |
| ·9578           | 30                                 | ·8863           | 64                                 | ·8001           | 98                                 |
| ·9560           | 31                                 | ·8840           | 65                                 | ·7969           | 99                                 |
| ·9544           | 32                                 | ·8816           | 66                                 | ·7938           | 100                                |
| ·9528           | 33                                 | ·8793           | 67                                 |                 |                                    |

Alcohol is extremely inflammable, and burns with a pale bluish flame, scarcely visible in bright daylight; but the heat of its flame is very intense, as may be shown by suspending in it a coil of fine platinum wire, which becomes white-hot. (p. 127.) It occasions scarcely any fuliginous deposition upon cold substances held over it. When it is diluted with a little water its flame is more blue and pale, and it occasions no trace of carbonaceous deposit. The products of the combustion of alcohol are carbonic acid and water, the weight of the water considerably exceeding that of the alcohol consumed. According to Saussure, jun., 100 parts of alcohol afford, when burned, 136 parts of water, the production of which may be shown by substituting the flame of alcohol for that



of hydrogen, in the apparatus, fig. 264 (p. 303), and if the tube at its extremity be turned down into a glass jar, it will be found that a current of carbonic acid passes out of it, which may be rendered evident by lime-water, and the extinction of a taper.

When alcohol is burned at a lower temperature than that required for its inflammation, as by the action of spongy or finely divided platinum, (*catalytic platinum*, p. 1060), or by a hot platinum wire, as described at p. 129, (fig. 116,) the products of its combustion are very different; the proportion of carbonic acid is less, and aldehydic and acetic compounds are formed.

There are many substances which communicate *color* to the flame of alcohol; from boracic acid it acquires a green tint; nitre, and the soluble salts of baryta, cause it to burn yellow; the soluble salts of strontia give it a beautiful rose-color, and chloride of calcium also reddens its flame; cupreous salts impart a fine green tinge. The curious monochromatic effect of common salt has been above adverted to (p. 128, *note*).

Graham has shown that alcohol may, in many instances, be combined with saline bodies, forming, as it were, a substitute for water of crystallization. Such combinations have been called *alcohates*. They are obtained by dissolving the substances by heat in absolute alcohol, and are deposited as the solution cools, more or less regularly crystallized. They appear to be definite compounds, and in some of them the alcohol is retained by an attraction so powerful, as not to be evolved at a temperature of  $400^{\circ}$  or  $500^{\circ}$ . Graham has examined the alcoholic combinations of chloride of calcium, nitrate of magnesia, nitrate of lime, chloride of zinc, and chloride of manganese. (*Quart. Journ.*, N.S., Dec., 1828; *Edinb. Phil. Trans.*, xi. 182.)

The action of chlorine and other halogens on alcohol we shall consider amongst *ethers*. It dissolves nearly all the acids, giving rise to an important and varied class of compounds, resulting from their mutual action: these also will be described in the section relating to *ether*.

There are a series of curious phenomena, arising out of the mere mixture of alcohol and acids, first observed by Chevreul, and subsequently examined by Pelouze. When a little sulphuric acid, for instance, is mixed with alcohol, the mixture has no action upon any *neutral* carbonate, and yet it decomposes acetate of potassa, evolving acetic acid. A mixture of alcohol and hydrochloric acid does not act upon carbonate of potassa, but it decomposes the carbonates of soda, lime, strontia, and magnesia. A mixture of alcohol and nitric acid is without action upon carbonate of potassa, but it acts powerfully on carbonate of lime, and of strontia, and slowly on carbonate of soda, baryta, and magnesia. Alcoholic solutions of acetic, and of tartaric acid, decompose none of the carbonates: a similar solution of citric acid decomposes carbonate of potassa and of magnesia, but not carbonate of baryta, strontia, or lime; and the alcoholic solution of oxalic acid decomposes carbonate of strontia, of lime, and of magnesia, but not carbonate of potassa. The addition of a small quantity of water does not affect these mixtures, for when a saturated solution of carbonate of potassa is mixed with the alcoholic solution of acetic acid, the carbonate is precipitated without effervescence: an alcoholic solution, therefore, may appear neutral to certain tests, whilst, in reality, strongly acid. It is difficult to suggest an explanation of these statements.

Alcohol dissolves a small quantity of sulphur, especially at its boiling temperature, but the greater portion is deposited, on cooling, in small brilliant crystals: the solution has a peculiar odor. When a flask of alcohol is suspended in the head of an alembic, containing sulphur, and the latter melted, so that as its vapor rises, it may be condensed with that of the alcohol, a reddish-yellow liquid passes over, containing sulphuretted hydrogen: this solution becomes milky upon the addition of water, and appears to contain about a hundredth part of sulphur. (LAURAGUAIS. *Mém. de l'Acad.*, 1758, p. 9.) A very similar solution may be obtained by passing sulphuretted hydrogen into alcohol, under slight pressure. Alcohol also dissolves phosphorus, taking up about a 240th part at its boiling-point, and retaining a 320th part when cold. This solution is luminous in the dark on exposure to air, and produces a beautiful pale, but ineffectual flame, when poured upon hot water. Alcohol dissolves sulphuret of carbon, and the solution is decomposed by the alkalis (see p. 524).

Potassium and sodium slowly decompose alcohol at common temperatures; heated with it, they evolve carburetted hydrogen. Potassa and soda are soluble in alcohol, and it is sometimes resorted to as a means of the purification of those alkalis; after a time, however, they begin to act upon each other, and complicated changes ensue; carbonate of the alkali is formed, and carbonaceous matter is evolved on the application of heat; by their slow mutual action acetic acid, a resin, and a species of brown extractive, appear to be formed. Ammonia and its carbonates are soluble at common temperatures in alcohol: it also absorbs a large quantity of ammoniacal, and of several other gases. Lithia, baryta, strontia, and lime, are almost insoluble in alcohol, even in their hydrated states; so also are the fixed alkaline carbonates: their sulphurets are soluble. The greater number of the chlorides, iodides, and bromides, which are soluble in water, are soluble also in alcohol, and with many of them the definite alcoholized compounds above mentioned are produced: thus there are definite compounds of chlorides of calcium, zinc, manganese, &c., with alcohol (*alcohates*), which have been described under those metals: the same is the case with some of the nitrates; but the sulphates are almost all insoluble; hence the use often made in the analysis of mixtures of salts, of the separative power of alcohol.

The mutual action of chloride of platinum and alcohol has been studied by Zeise, and his inquiries seem to show the existence of a peculiar class of salts, of which hydrocarbon and the chlorides are the elements; he terms them *etherized salts*. (*Poggend. Ann.*, xxi. 497.) Hellot a long time ago obtained a crystallizable compound of chloride of antimony and alcohol; and more lately Lewy has described an analogous compound of perchloride of tin and alcohol. (*Ann. Ch. et Ph.*, 3ème Sér., March, 1846.)

The uses of alcohol in the arts, and its applications to various economical purposes, are extremely numerous: to the chemist it is a most valuable species of fuel, but we are almost debarred from its use by its high price; and for the same reason many manufactures, in which alcohol is an essential agent, cannot be productively carried on in this country. Its solvent powers, in regard to resins, oils, and other organic products, have been elsewhere noticed: its medicinal and pharmaceutical employ-



ment is also important; and it is an agreeable exhilarant in wine, beer, and other fermented liquors: the mischief, on the other hand, which results from its improper use, is very extensive, as illustrated in the broken constitution of mind and body which characterizes the dram-drinker and the habitual drunkard.

*Decomposition and Component Parts of Alcohol.*—When alcohol is passed through a red-hot tube it is decomposed, more or less perfectly according to the temperature, and to the rapidity of its passage: the most accurate experiments upon this subject are those of T. de Saussure (*Ann. de Chim.*, xlii. and lxxxix.); he passed the vapor of alcohol slowly through a red-hot porcelain tube; there was deposited upon its interior a little charcoal, a volatile crystalline substance (probably naphthaline), and a brown empyreumatic oil; and gas was evolved, the specific gravity of which was 0.586, and which was a mixture of carburetted hydrogen, carbonic oxide, and hydrogen.

When alcohol vapor and oxygen are mixed in proper proportions, and fired by an electric spark, a violent explosion ensues, and carbonic acid and water are the results: 1 volume of alcohol vapor requires 3 volumes of oxygen for its perfect combustion, and the result is, 2 volumes of carbonic acid, and 3 volumes of aqueous vapor.

Dumas and Boullay analyzed alcohol by oxide of copper (*Ann. Ch. et Ph.*, xxxvi. 294), and the results of their experiments, with those of other analysts (corrected for absolute alcohol), give the following as the composition of this fluid:—

|                        |   |     |    |     |        | Saussure. | Dumas and Boullay. |
|------------------------|---|-----|----|-----|--------|-----------|--------------------|
| Carbon.....            | 4 | ... | 24 | ... | 52.18  | 51.98     | 52.17              |
| Hydrogen .....         | 6 | ... | 6  | ... | 13.04  | 13.70     | 13.31              |
| Oxygen .....           | 2 | ... | 16 | ... | 34.78  | 34.32     | 34.52              |
| <hr/>                  |   |     |    |     |        | <hr/>     | <hr/>              |
| Anhydrous alcohol .... | 1 |     | 46 |     | 100.00 | 100.00    | 100.00             |

The equivalent 46, which is here assigned to alcohol, is adopted in reference to the composition of *ether*, of which it is convenient to regard alcohol as a *hydrate*; so that ether being C<sub>4</sub> H<sub>5</sub> O, alcohol becomes C<sub>4</sub> H<sub>5</sub> O + HO (see *Ether*).

Alcohol has also been represented as a *hydrate of olefiant gas*, = 2[C<sub>2</sub> H<sub>2</sub>, HO], or, what amounts to the same thing, as binhydrate of etherine, or quadrihydrocarbon (see p. 485) = C<sub>4</sub> H<sub>4</sub>, 2HO.

These views of the composition of alcohol are confirmed by reference to the density of its vapor. According to Gay-Lussac, the experimental density is, as already stated, 1.613; and if this vapor be regarded as containing 8 volumes of carbon-vapor, 12 volumes of hydrogen and 2 volumes of oxygen, condensed into 4 volumes, which upon this authority is the combining measure of alcohol vapor, the theoretical density will be 1.6; for

|                              |         |
|------------------------------|---------|
| 8 volumes carbon vapor ..... | Sp. gr. |
| 12 „ hydrogen .....          | 3.372   |
| 2 „ oxygen.....              | 0.825   |
| <hr/>                        |         |
| 4 )                          | 6.402   |
| <hr/>                        |         |
|                              | = 1.600 |

ETHER. OXIDE OF ETHYLE.  $C_4H_5O = AeO$ .

The term *Ether* is now generally confined to a liquid obtained by the action of sulphuric acid upon alcohol, and which was formerly designated *sulphuric ether*. It is first described by Valerius Cordus, in 1540, who called it *oleum vitrioli dulce*. The name of *ether* was applied to it 190 years afterwards by Frobenius, who, in a paper in the *Philosophical Transactions*, described its singular properties; at the end of this paper is a note by Godfrey Hankwitz, Mr. Boyle's operator, mentioning the experiments that had been made upon it by Boyle and by Newton. (THOMSON. *Chem. of Inorganic Bodies*, ii. 296.) Since that period the process of etherification has been minutely studied.

*Production of Ether*.—1. Ether is usually obtained either by distilling a mixture of sulphuric acid and alcohol, or by suffering alcohol gradually to dribble into the heated, and somewhat diluted acid. Phillips gives the following directions for the former process:—"Mix with 16 ounces of sulphuric acid, an equal weight of rectified spirit, and distil about 10 fluid ounces; add 8 ounces of spirit to the residuum in the retort, and distil about 9 fluid ounces; or continue the operation until the contents of the retort begin to rise, or the product becomes considerably sulphurous; mix the two products, and if the mixture consist of a light and heavy fluid, separate them: add potash to the lighter, as long as it appears to be dissolved; separate the ether from the solution of potash, and distil about nine-tenths of it, to be preserved as *ether sulphuricus*, the specific gravity of which ought to be at most .750." (*Experimental Examination of the London Pharmacopœia*.)

Preparing ether upon a larger scale, it was found that 14 parts of alcohol (specific gravity .820), mixed with an equal weight of sulphuric acid (specific gravity 1.8), and submitted to distillation, afforded about 8 parts of impure ether (specific gravity .770). 7 parts of alcohol were then added to the residuum, and about  $7\frac{3}{4}$  parts more of impure ether drawn off. These products, when mixed, had a specific gravity of about .782, and when rectified by distillation over carbonate of potassa, afforded  $10\frac{1}{4}$  parts of ether, of a specific gravity of .735, and about  $3\frac{1}{2}$  parts of ethereal spirit, which was employed, instead of an equal quantity of alcohol, in the next operation.

These processes, when carried on on a small scale, may be conducted in glass retorts with adopters and cooled receivers; but upon the large scale, a leaden still or alembic is most convenient. The ether-apparatus employed at Apothecaries' Hall, consists of a leaden still, heated by means of high-pressure steam carried through it in a contorted leaden pipe; a tube enters the upper part of the still, for the purpose of suffering alcohol gradually to run into the acid in a way which I shall presently explain. The still-head is of pewter, and is connected by about 6 feet of tin pipe, with a very capacious condensing apparatus, duly cooled by a current of water; the receivers are of pewter with glass lids, and have a side tube to connect them with the delivering end of the condensing-pipe. In conducting this operation, too much caution cannot be observed in avoiding



the proximity of fire, and the use of fragile vessels; in all cases in which ether is to be dealt with these cautions cannot be too strictly enforced, as will be evident when its properties are stated. One of the great advantages in using steam as the source of heat is, that it obviates the necessary vicinity of fire.

2. Boullay's process for the production of ether, which is an improvement upon the preceding, is as follows, (*Gilbert's Annalen*, xxxiv. 270; *Ann. Ch. et Ph.*, xxxvi. 294:) equal parts of sulphuric acid and of alcohol (specific gravity  $\cdot 837$ ) are cautiously mixed in a tubulated retort connected with a tubulated receiver by means of a condensing adopter; the retort is placed in a sand-heat, and the receiver cooled by the proper application of water. An S tube passes air-tight through the tubulature of the retort, the lower end of which is drawn out into a very small or almost capillary opening, and so adjusted as to dip to about two-thirds of the depth of the liquid in the retort; heat is then applied by the sand-bath till the contents of the retort just begin to appear to boil; the fire is then slackened, or damped, so as to keep up a regular ebullition, and as the apparatus is air-tight, the expansion within is suffered to escape by a siphon tube, which passes through the tubulature of the receiver. When about 2 parts of product have passed over, an equal quantity of alcohol is so gradually suffered to trickle into the retort by the S tube, as not to check ebullition, but to compensate for that which distils over. When, in this way, a quantity of alcohol has been added, equal to that contained in the original mixture, the operation is generally left to itself, and as soon as white vapors, and drops of oil appear in the adopter, the fire is withdrawn. The products of this distillation are usually divided into three parts; the first is alcohol with a little ether, which first passes over; the second, and largest, or ethereal, portion, is mixed with a sixteenth of its weight of carbonate of potassa, which abstracts water and sulphurous acid, and decomposes any oil of wine that may chance to be contained in it; this mixture is shaken, and when the ether has acquired a sweet and pure odor, it is rectified by slow distillation from a water-bath, till two-thirds of its original bulk have distilled over; this portion is pure ether. The residue of the rectification is mixed with the last portion of the original distillation, and kept for some days in contact with the carbonate of potassa before used, and a little water and peroxide of manganese are added so as to get rid of the sulphurous acid; when this is done, the stratum of ether is drawn off and rectified, but it never equals in quality that of the former part of the process.

It will be observed that, in this process, a large additional quantity of alcohol is gradually added, and converted into ether by the original portion of sulphuric acid: and by obvious contrivances, the same thing may be effected with the still and apparatus used on the large scale.

3. Mitscherlich (in the first volume of his *Lehrbuch der Chemie*) has added some important facts to the preceding details, and has given a form of apparatus for the production of ether which well illustrates it. It consists of a large flask or bolthead, the mouth of which is closed with a cork having three perforations, one of which allows the insertion of a thermometer by which the temperature of the contents of the flask can be regulated; the second admits of the passage of a small tube termi-

nating at its upper end in a funnel, and at its lower, within the flask, in a capillary opening which dips into the liquid; from the third aperture a tube issues for the conveyance of the vapors generated within the flask into a proper condenser immersed in cold water; the end of this tube within the flask is slanted off, so that liquid forming in it may drop back into the flask and not obstruct the free egress of the vapor. Absolute alcohol is first poured into the flask, and then sulphuric acid, somewhat diluted, is gradually added, care being taken to prevent the heating of the mixture above  $250^{\circ}$  ( $120^{\circ}$  Cent.). The proportions are, 100 parts of sulphuric acid (which already contains 18.5 of water) diluted with 20 parts of water, and mixed with anhydrous alcohol, in the proportion of 50 parts to every 100 of concentrated acid. To this mixture heat is applied, and it is kept boiling till the thermometer within the flask indicates  $284^{\circ}$  ( $140^{\circ}$  Cent.); two strips of paper are then pasted upon opposite sides of the flask to indicate exactly the bulk of its contents, by showing the level of the liquid within it; alcohol is then suffered to flow in by the funnel-tube, the supply being so regulated as to maintain the boiling-point at  $284^{\circ}$ . If, having set out with 9 ounces of sulphuric acid,  $1\frac{1}{5}$  oz. of water, and 3 ounces of alcohol, *in the flask*, the specific gravity of each successive 2 ounces that pass over into the receiver attached to the condenser be determined, that of the first 2 ounces will be 0.780, that of the two following 0.788, and this gradually increases to 0.798, at which the density generally arrives by the ninth or tenth ounce, and then remains constant; that being nearly the density of the alcohol used.

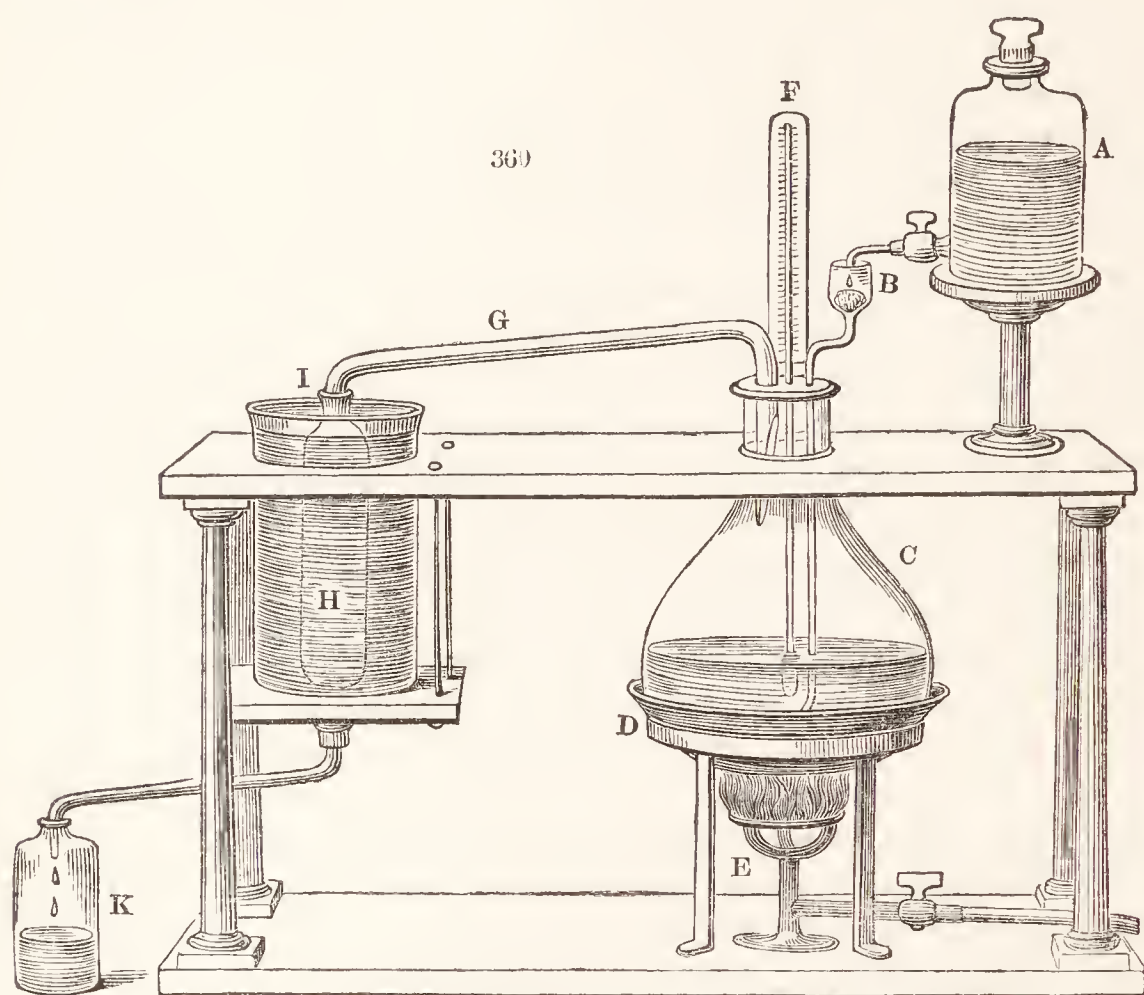
If the precaution just stated respecting the adjustment of the temperature be strictly attended to, any quantity of alcohol may be etherized by the same portion of acid, which is no further altered than by foreign matters which may be accidentally present, or by the volatilization of a minute portion along with the ethereal vapor.

The liquid which passes over through the condensing apparatus into the receiver, separates into two parts, the lighter stratum being ether, with a little alcohol and water; and the heavier, water, with a little alcohol and ether; and when the process has been carefully conducted, the weight of these products exactly corresponds with that of the alcohol consumed. In an experiment in which a large quantity of product had been obtained, it was found to consist of 65 ether, 18 alcohol, 17 water; now the quantity of water which should have been evolved in the production of 65 parts of ether is 15.4; so that the practical is as near to the theoretical result as could be expected, considering the impossibility of preventing the loss of ether by evaporation, and including errors of experiment. Careful manufacturers obtain from 100 parts of spirit of wine, containing 76 parts by weight of anhydrous alcohol, 60 parts of ether of the specific gravity 0.727; according to calculation, they should obtain 58 parts of ether of 0.724. With this diluted alcohol, the water which passes over is of course in greater quantity than when absolute alcohol is used.

4. The following apparatus and process answers well for the preparation of ether upon the large or small scale. A is the alcohol-holder; it has a grooved stopper, so that when the stop-cock is turned, the alcohol may be allowed to drop with any degree of rapidity into the funnel B, the



tube of which is elongated, and terminates by a small aperture near the bottom of the flask *c*, which is placed in a copper bath or sand heat, and may be heated up to any required temperature by the gas-burner *E*. *F* is a thermometer properly graduated for showing the temperature of the liquor in the flask. *G* is a glass tube of a sufficiently capacious bore for the conveyance of vapors from the flask to the condenser *H*, which is surrounded by cold water in the vessel *I*, and delivers its contents into the receiver *K*.



In using this apparatus, a mixture of 8 parts by weight of concentrated sulphuric acid, and 5 parts of rectified spirit of wine of sp. gr. 0.834 is introduced into the flask, and heated by means of the lamp till it boils, and attains a temperature of  $300^{\circ}$ . Alcohol is then suffered to drop in through the long funnel, and by adjusting its quantity on the one hand, and regulating the degree of heat on the other, by the gas burner, the temperature of  $300^{\circ}$  is maintained as steadily as possible, taking care at the same time that the liquor in the flask is kept in rapid ebullition. Under these circumstances the bulk of this liquor may be maintained uniform for several hours, and every drop of alcohol which falls in, is converted into ether and water, the mixed vapors of which pass through the tube *G* into the condenser; and the receiver *K* is ultimately filled with water and ether, the latter floating upon the former.

The leading point to be attended to in this operation is the maintenance of a steady temperature at or about  $300^{\circ}$ , and of rapid or even violent ebullition. The limits of the ether-producing temperature are between  $260^{\circ}$  and  $310^{\circ}$ , and the success of the operation is pretty well ensured by the use of oil of vitriol and spirit of wine, in the above proportions, and of the described strength. If more alcohol, or a weaker acid be used, so as

to occasion the boiling-point to fall below  $260^{\circ}$ , little else than unchanged alcohol distils over; and if, by the employment of too much oil of vitriol, the boiling-point rises up to, or above  $320^{\circ}$ , in that case *olefiant gas* is generated, together with variable quantities of other products.

The ether of commerce almost always contains alcohol, which materially affects its density; sometimes it also contains water, which is the case with what is termed *washed ether*; and if ether has been long prepared, it is often slightly acid, and leaves a peculiar odor when rubbed upon the hand. In order to procure from it perfectly *pure ether*, it must be well shaken in a close vessel with about twice its bulk of water, and allowed to separate upon the surface of the mixture; it is then poured off, and a sufficient quantity of well-burned lime added to it, by which the water which it had acquired by the agitation is abstracted; the mixture of ether and lime is then distilled, care being taken to prevent all escape of vapor, and to keep the condensing-receivers cold; the first third that distils over may be considered as *pure ether*, free from alcohol and from water. Commercial ether may also be purified by agitating it with milk of lime, and then distilling it from a water-bath by a gentle heat: this first distillate is then shaken with water to separate alcohol, and the resulting aqueous ether subsequently dehydrated by distilling it off quicklime, or chloride of calcium.

*Properties of Ether.*—Ether is a highly volatile\* transparent, colorless, limpid liquid, of a peculiar penetrating and agreeable odor, and a pungent and sweetish taste; it is highly exhilarating, and produces a remarkable species of intoxication when its vapor is respired mixed with air, so that by the proper management of the inhalation, a continuous insensibility to pain may be maintained. This application of ethereal vapor has lately been extensively resorted to in the performance of surgical operations, and various forms of inhalers have been invented for the purpose. (See descriptions and representations of these in the *Pharmaceutical Journal*, vii. 13.) Ether is neither acid nor alkaline; it has a high refractive power in regard to light; it is a non-conductor of electricity.

The specific gravity of ether, at  $68^{\circ}$ , is, according to Saussure, 0.715; according to Gay-Lussac its specific gravity (in reference to water at its maximum density) at  $90^{\circ}$  is 0.69739; at  $76^{\circ} = 0.71192$ ; at  $68^{\circ} = 0.7154$ ; and at  $54^{\circ} = 0.7237$ . Assuming the water at the same temperature as the ether, its specific gravity at  $68^{\circ}$  is  $= 0.71654$ ; and at  $58^{\circ}$  it is  $= 0.7240$ . According to Dumas and Boullay the specific gravity of ether at  $68^{\circ}$  is  $= 0.713$ . This exactly agrees with my own determination of the specific gravity of ether at  $60^{\circ}$  which had been washed and distilled off quicklime.

At mean pressure, ether boils, according to Gay-Lussac, at  $96.5^{\circ}$ . Ether of the specific gravity of .720 may be said to boil under a pressure of 30 inches, at  $98^{\circ}$ . Upon this subject, however, authorities vary a

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\* See the experiments at pp. 74 and 82, (figs 84 and 91,) in reference to the low boiling-point, and the cold produced by the evaporation of ether. When a few drops of ether covering a drop of water are blown upon by a blow-pipe, the water freezes in

consequence of the rapid evaporation of the ether. It is obvious that were it not for atmospheric pressure we should only know ether as a gas or vapor, for in vacuo it boils at all temperatures.



little, in consequence of variations in the density of the ether, and also of barometrical pressure, circumstances which easily influence the boiling-point of this liquid; it is also much affected by the nature and cleanliness of the vessel in which the experiment is made. Dr. Bostock found that, in a clean glass tube, it might be heated considerably above its boiling-point, but that when in that state a few metal filings or other solid particles were thrown into it, its temperature instantly fell, and it entered into ebullition. (*Ann. of Phil.*, 2nd Series, viii. 296.) The extreme volatility of ether renders it impossible to pour it from one vessel to another without losing a portion by evaporation, and its vapor, in consequence of its density, is easily discerned passing off from the liquid: it is this which renders it so dangerous to expose ether near to, and especially above, the flame of a candle. This density of ether vapor is well shown by dipping a flock of cotton into ether, and placing it within a glass tube of about an inch diameter, and 18 or 20 inches long; the vapor will descend and escape from the lower end of the tube, where it may be inflamed by a lighted taper, but none rises to the upper end of the tube. If the lower end of the tube be drawn into a point and bent upwards, the ether vapor may there be burned in the manner of a gas-light.

The great density of the vapor of ether was first noticed by Dr. Ingenhouz. (*Nouvelles Expériences*, p. 180.) Experiments have been made upon this subject by Dalton (*Manchester Mem.*, 2nd Series, iii. 260) and by Gay-Lussac and Despretz. (*Ann. Ch. et Ph.*, i. 218, and xxi. 143.) The results of the latter experimentalists closely agree, and place the density of ethereal vapor, at mean pressure and temperature, between 2·5808 and 2·5860 in reference to air as = 1. At the temperature of 212° 1 volume of ether gives 212 volumes of vapor.

The elastic force of ether vapor is shown by letting a drop or two of ether pass up into the vacuum of a barometer, when it instantly depresses the mercury several inches, more or less, according to the temperature: hence also, when thrown up into gases standing over mercury, it greatly augments their bulk. The following table shows the result of Dalton's experiments on the force of ether vapor at different temperatures.

| Temp.     | Force of Ethereal vapor. | Temp.      | Force of Ethereal vapor. |
|-----------|--------------------------|------------|--------------------------|
| 36° ..... | 7·5 inches.              | 173° ..... | 120·0                    |
| 64 .....  | 15·0                     | 212 .....  | 208·0                    |
| 96 .....  | 30·0                     | 220 .....  | 240·0                    |
| 132 ..... | 60·0                     |            |                          |

The volume of liquid ether is extremely affected by change of temperature; much more so than that of alcohol. The following are the results of Gay-Lussac's experiments upon this subject, in which the volume of ether, at its boiling-point, is assumed = 1·000.

| Cent.        | Fahr.     | Bulk.  | Cent.         | Fahr.     | Bulk. |
|--------------|-----------|--------|---------------|-----------|-------|
| 35·66° ..... | 95° ..... | 1000·0 | 5·66° .....   | 42° ..... | 953·6 |
| 30·66 .....  | 87 .....  | 991·9  | 0·66 .....    | 33 .....  | 948·0 |
| 25·66 .....  | 76 .....  | 983·8  | — 4·33 .....  | 26 .....  | 941·3 |
| 20·66 .....  | 69 .....  | 975·8  | — 9·33 .....  | 14 .....  | 934·5 |
| 15·66 .....  | 60 .....  | 968·2  | — 14·33 ..... | 4 .....   | 928·0 |
| 10·66 .....  | 51 .....  | 960·9  | — 19·33 ..... | 3 .....   | 922·0 |

According to Fourcroy and Vauquelin, ether congeals or crystallizes when cooled down to  $-46^{\circ}$  (*Ann. de Ch.*, xxix. 289), but neither Thenard nor Bussy were able to freeze it, so that the ether used by the former experimentalists was probably impure. Faraday also failed in congealing ether, though exposed to a temperature of  $166^{\circ}$  below  $0^{\circ}$ . (*Phil. Trans.*, 1845, p. 158.)

From the experiments of Gerard it appears that ether passes more readily through a capillary orifice than water, and water than alcohol; the relative times for equal measures of each fluid, at the temperature of  $54^{\circ}$ , being 101" for ether, 349" for water, and 856" for alcohol. The comparative heights to which these three fluids rose in the same capillary tube were = 6 for ether, 9 for alcohol, and 13 for water. (*Ann. de Ch. et Ph.*, vi. 239.)

When ether is inflamed it burns away with a bright and slightly sooty flame, leaving no residue, and producing carbonic acid and water\*. By passing ether into a jar supplied with a jet and stop-cock, standing over warm water, its vapor may be burned at the jet: if its vapor be mixed with about 10 volumes of oxygen it explodes violently by an electric spark, but with smaller quantities of oxygen, or with air, this combustion is only imperfect; and if a little ether be poured into a bladder full of air, and supplied with a stop-cock and jet, the mixture of air and ether vapor may be burned at the jet without risk of explosion.

Exposed to air and light, as in bottles which are frequently opened, ether becomes less perfectly volatile, and less capable of dissolving fixed oil, in consequence of the formation of a little acetic acid. The presence of this acid is not at first apparent, because it forms acetic ether, but it gives the ether a peculiar odor, and in time it becomes acid to tests. (PLANCHE, *Ann. de Ch. et Ph.*, ii. 273.) The best way of preserving ether is to keep it in small well-stopped bottles, or even in sealed tubes, and in a dark place. Gay-Lussac, in some very old ether, which had been occasionally exposed to air, and the boiling-point of which was elevated to  $130^{\circ}$ , found an oily matter, crystallizable, and of an ethereal odor.

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\* When ether vapor is passed over red-hot platinum wire, or consumed in the lamp without flame (p. 129, figs. 116 and 117), an acid is produced, which was first examined by Daniell. (*Quart. Jour. of Science and Arts*, vi. 318.) He obtained it by placing the lamp, filled with ether, and properly trimmed with a coil of glowing platinum wire, under the head of an alembic, in which the vapor was condensed, and collected in a phial applied to its beak. *Lampic acid*, for so he termed this product, is colorless, sour, and pungent; its vapor is very irritating, and its specific gravity, when purified, about 1.015. It reddens vegetable blues, and decomposes the alkaline carbonates with effervescence. When added to the solutions of silver, gold, platinum, mercury, and copper, and the mixture heated, the metals are thrown down in the metallic state. On distilling *lampate*

*of mercury*, made by digesting peroxide of mercury in the acid, the lampic acid passes over in the form of a very dense liquid with an intensely suffocating odor. These properties first induced Daniell to consider this product as a peculiar acid, but upon further inquiry into its nature and combinations (*Quart. Jour.*, xii. 64), he found the acid to be the acetic, combined with a compound of carbon and hydrogen, differing from alcohol and from ether, and conferring upon it those properties, in respect to certain metallic solutions, which have been just mentioned. The more recent researches of Döbereiner and Liebig have shown that this acid is identical with the compound which they have termed *aldehydic* or *acetulous acid*, and which will be subsequently described. Formic and acetic acids are also at the same time produced.



According to Döbereiner, ether which has been exposed to air, contains free nitrogen, the oxygen having combined with the ether.

Ether is soluble to a certain extent, in water, of which 9 parts take up 1 of ether; and washed ether retains about a tenth part of water; or, according to Liebig, 36 parts of pure ether dissolve only 1 part of water.

When a little ether is introduced into chlorine, the gas is absorbed, and peculiar compounds result, which we shall afterwards examine; when bubbles of chlorine are passed into ether, they often cause inflammation, and when a small quantity of ether is poured into a large jar of gaseous chlorine, previously warmed, it occasionally happens that a considerable explosion ensues. If the ether be cooled, and chlorine passed into it, hydrochloric acid is formed, together with a fluid compound containing chlorine, which, when saturated with potassa, produces chloride of potassium and acetate of potassa. (MALAGUTI, *Ann. Ch. et Ph.*, 3ème Sér., Jan., 1846.) Ether absorbs a large quantity of hydrochloric acid gas, and the compound yields *chloride of ethyle* (which see) when distilled.

Iodine and bromine are soluble in ether, and gradually react upon and decompose it. The solution of iodine in ether is dark brown, and soon gives rise to the production of hydriodic acid. The action of bromine upon ether has been studied by Löwig. (*Ann. Ch. et Ph.*, Lxi. 279.) When ether is saturated with bromine, and the mixture left for ten or twelve days, it is entirely decomposed; the products are, 1, formic acid? 2, hydrobromic acid; 3, hydrobromic ether; 4, heavy bromic ether; 5, bromal; the four first products may be separated by distillation, and the *bromal* remains; it may be purified by mixture with water, and in the course of twenty-four hours crystals of *hydrated bromal* are formed.

Bromal is composed of

|                |   |       |     |       |        |             |
|----------------|---|-------|-----|-------|--------|-------------|
|                |   |       |     |       |        | Löwig.      |
| Carbon .....   | 4 | ..... | 24  | ..... | 8.71   | ..... 8.64  |
| Hydrogen ..... | 1 | ..... | 1   | ..... | 0.36   | ..... 0.38  |
| Oxygen .....   | 2 | ..... | 16  | ..... | 5.80   | ..... 6.33  |
| Bromine .....  | 3 | ..... | 234 | ..... | 85.13  | ..... 84.65 |
| <hr/>          |   |       |     |       |        | <hr/>       |
| Bromal .....   | 1 |       | 275 |       | 100.00 | 100.00      |

*Hydrated bromal* consists of

|                                      |   |       |     |       |       |
|--------------------------------------|---|-------|-----|-------|-------|
| Bromal .....                         | 1 | ..... | 275 | ..... | 88.5  |
| Water .....                          | 4 | ..... | 36  | ..... | 11.5  |
| <hr/>                                |   |       |     |       |       |
| Crystallized hydrate of bromal ..... | 1 |       | 311 |       | 100.0 |

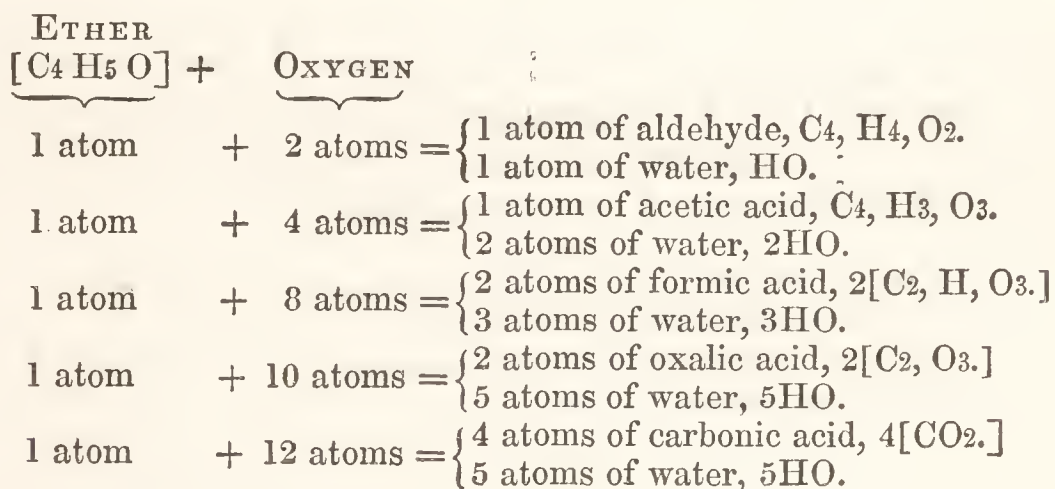
When hydrate of bromal is boiled with an alkaline solution, 2 atoms are resolved into 2 atoms of formic acid, 2 of bromoform, and 6 of water. The details of the other actions of chlorine, iodine, and bromine upon ether and alcohol, are given further on.

Ether dissolves a small quantity of sulphur (1-80th), which is not thrown down by the addition of a little water; the solution smells of sulphuretted hydrogen, and by slow evaporation deposits regular crystals of sulphur. It acquires acidity by exposure to air. I once had occasion to saturate about a pint of ether with sulphuretted hydrogen gas; the solution was put aside in a well-stopped bottle for some months, and had

then deposited small octohedral crystals of sulphur. Ether dissolves more than 2 per cent. of phosphorus (1-37th); the solution, when concentrated by evaporation, deposits crystals of phosphorus; it is luminous in the dark when in contact of air; and, poured upon hot water, produces a brilliant column of luminous vapor. Exposed to air this solution becomes sour; it deposits phosphorus when mixed with water or with alcohol; and it gradually deposits a red matter, especially when exposed to light.

A small quantity of sulphuric acid added to ether produces no effect, but a mixture of equal parts of ether and the acid blackens, and yields, on distillation, oil of wine, olefiant gas, acetic and sulphurous acid, and water; it leaves a resinous matter and charcoal. Anhydrous sulphuric acid decomposes ether, and produces, according to Liebig, "isæthionic and althionic acids, oil of wine, and sulphate and bisulphate of oxide of ethyle; if heat be used, these products are decomposed, and sulphate of oxide of ethyle, oil of wine, water, and ether, together with acetic, formic, and sulphurous acids, carbonic oxide, and olefiant gas, pass over."

Heated with nitric acid, ether yields carbonic, acetic, formic, and oxalic acids, and aldehyde. The following, according to Liebig, are the results of this action of nitric acid on ether.



Ammoniacal gas is abundantly absorbed by ether. Potassa and soda act feebly upon it, and give rise, among other products, to acetic and formic acids, which unite to the alkali. Potassium and sodium are slowly converted into potassa and soda when kept in ether, and hydrogen is disengaged; but the mutual action of these substances has not been accurately studied. The easily oxidizable metals, when kept in ether, such as lead, zinc, iron, and tin, are, according to Berzelius, slowly oxidized, and form acetates. Many salts are also soluble in ether, and especially the chlorides of gold, platinum, iron, and uranium; the property which ether has of abstracting these salts from their aqueous solutions has been adverted to under the history of the respective metals. Ether appears to form a definite crystalline compound with perchloride of tin, = 2[C<sub>4</sub> H<sub>5</sub> O] + Sn Cl<sub>2</sub>. (KUHLMANN. LEWY. *Ann. Ch. et Ph.*, March, 1846. 309.)

The fixed and volatile oils, many of the resins, caoutchouc, various forms of extractive, the alkaloids, and some other vegetable principles, are more or less soluble in ether; hence ether is often employed in the analysis of organic products, as a means of separating their proximate principles from each other.



Alcohol and ether mix in all proportions, and, as above stated, the ether of commerce generally contains alcohol, which affects its density and its boiling-point: the means of abstracting the alcohol have been before mentioned. *Hoffman's anodyne liquor*, and the *spirit of ether* of Pharmacy, are such alcoholic solutions. When water, alcohol, and ether, are shaken together, the mixture separates into two layers, each of which contains the three liquids; in the uppermost there is excess of ether, and in the lowermost excess of water. By the further addition of alcohol, the sp. gr. of the upper layer may be brought to 0·82, and that of the lower to 0·92, after which an increase of alcohol produces a homogeneous mixture.

The following table of the density of various mixtures of ether (specific gravity 0·720) with alcohol (specific gravity 0·830), was constructed from direct experiments, by Dalton.

| Ether. | Alcohol. | Sp. Gr. | Ether. | Alcohol. | Sp. Gr. |
|--------|----------|---------|--------|----------|---------|
| 100    | + 0      | 0·720   | 40     | + 60     | 0·792   |
| 90     | + 10     | 0·732   | 30     | + 70     | 0·804   |
| 80     | + 20     | 0·744   | 20     | + 80     | 0·816   |
| 70     | + 30     | 0·756   | 10     | + 90     | 0·828   |
| 60     | + 40     | 0·768   | 0      | + 100    | 0·830   |
| 50     | + 50     | 0·780   |        |          |         |

*Composition of Ether.* When the vapor of ether is slowly passed through a red-hot tube, it is decomposed, and resolved into water, aldehyde, and carburetted hydrogen gases. According to Liebig, 3 atoms of ether, = C<sub>12</sub> H<sub>15</sub> O<sub>3</sub>, thus decomposed, yield

|                                      |  |
|--------------------------------------|--|
| 3 atoms of olefant gas               | C 6 H 6  |
| 2 atoms of light carbo-hydrogen..... | C 2 H 4  |
| 1 atom of aldehyde .....             | C 4 H 4 O <sub>2</sub>                         |
| 1 atom of water .....                | H O  |
|                                      | <hr/>  |
|                                      | C <sub>12</sub> H <sub>15</sub> O <sub>3</sub> |

Analyzed by passing it through red-hot oxide of copper, ether furnishes the following elementary composition:—

|          |   |       |       |       |        | Dumas and<br>Boullay. |
|----------|---|-------|-------|-------|--------|-----------------------|
| Carbon   | 4 | ..... | 24    | ..... | 64·87  | ..... 65·0            |
| Hydrogen | 5 | ..... | 5     | ..... | 13·51  | ..... 13·8            |
| Oxygen   | 1 | ..... | 8     | ..... | 21·62  | ..... 21·2            |
| <hr/>    |   |       | <hr/> |       | <hr/>  | <hr/>                 |
| Ether    | 1 |       | 37    |       | 100·00 | 100·0                 |

The specific gravity of *ether vapor* has been shown to be 2·580, and with this, in reference to the above analysis, its calculated density is consistent, for according to Gay-Lussac, a volume of the vapor of ether includes

|                                       |         |
|---------------------------------------|---------|
|                                       | Sp. Gr. |
| 4 vols. of carbon vapor [ ·422 × 4 ]  | = 1·688 |
| 5 vols. of hydrogen gas [ 0·069 × 5 ] | = 0·345 |
| $\frac{1}{2}$ vol. of oxygen.....     | = 0·550 |
| <hr/>                                 | <hr/>   |
| 1 vol. of ether vapor .....           | 2·583   |

Assuming that view of the composition of alcohol and of ether which represents the former as a *binhydrate*, and the latter as a *hydrate of etherine*, we have

46 parts of Alcohol, composed of

|                                  |                                |
|----------------------------------|--------------------------------|
| 1 equivalent of Etherine<br>= 28 | 2 equivalents of Aqueous Vapor |
| $9 \times 2 = 18$                |                                |

$$28 + 18 = 46$$

Resulting  
volume  
of  
Alcohol  
Vapor.

37 parts of Ether consist of

|                                  |                                   |
|----------------------------------|-----------------------------------|
| 1 equivalent of Etherine<br>= 28 | 1 equivalent of Aqueous Vapor = 9 |
|----------------------------------|-----------------------------------|

$$28 + 9 = 37$$

Resulting  
volume of  
Ether  
Vapor

In either view of this subject it is obvious that alcohol is convertible into ether, by the removal of one-half of its elementary oxygen and hydrogen, which are in the proportions that form water.

Berzelius has adopted a view of these subjects, to which I have elsewhere adverted, and which consists in regarding ether as the oxide of an *organic metalloid*, or *compound inflammable basis*, or *radical*, which he terms *ethyle* or *ethule*, (from *ether* and  $\upsilon\lambda\eta$ , *principle*,) and which, from reference to the preceding results, will obviously consist of 4 atoms of carbon and 5 of hydrogen, and be represented therefore by the equivalent 29, (or,  $6 \times 4 = 24 + 5$ ,) and *ether* will contain 29 ethyle + 8 oxygen, and be represented by the equivalent 37. According to this view, alcohol is a *hydrate of oxide of ethyle*, or of *ether*, consisting of 37 ether + 9 water = 46; and ether is represented as composed of

|                |   |     |    |     |        |                      |              |     |     |     |        |       |
|----------------|---|-----|----|-----|--------|----------------------|--------------|-----|-----|-----|--------|-------|
| Carbon .....   | 4 | ... | 24 | ... | 64.86  | } = Ethyle.....      | 1            | ... | 29  | ... | 78.39  |       |
| Hydrogen ..... | 5 | ... | 5  | ... | 13.53  |                      |              |     |     |     |        |       |
| Oxygen .....   | 1 | ... | 8  | ... | 21.61  |                      | Oxygen ..... | 1   | ... | 8   | ...    | 21.61 |
| <hr/>          |   |     |    |     |        |                      |              |     |     |     |        |       |
| Ether .....    | 1 |     | 37 |     | 100.00 | Oxide of ethyle .... | 1            |     | 37  |     | 100.00 |       |

But ethyle has not been isolated: in the *Philosophical Magazine* for 1839 (vol. xix., p. 543), a mode of obtaining it in a separate state is noticed by Löwig, but the process is not very intelligible, so that in the present state of our knowledge it must be considered as a *hypothetical radical*, of which ether is an oxide. *Ethyle* combines with the halogens, and *ether* combines with the oxyacids: combined with an atom of water, ether forms *alcohol*, which therefore is, as already stated, a *hydrate of oxide of ethyle*. This hypothetical view of the constitution of ether and of alcohol is now generally adopted, and is conveniently applicable to all the ethereal combinations, so that in reference to these, I shall assume 37 as the equivalent of ether, and 46 as the equivalent of alcohol.



*Theory of Etherification.* It will be evident from the details which have been given, that 1 equivalent of alcohol  $\equiv 46$ , is converted into 1 of ether and 1 of water; or that 1 volume of the vapor of ether, and 1 volume of aqueous vapor, are the results of the decomposition of 2 volumes of alcoholic vapor.

This important fact, namely, that alcohol is converted into ether by the abstraction of water, or its elements, was first demonstrated by Gay-Lussac, who conceived that the influence of the sulphuric acid consisted in this abstraction of water; and the well-known attraction of that acid for water seemed to sanction the conclusion, which was further strengthened by the fact, that a similar ether might be formed by the agency of arsenic, phosphoric, and fluoboric acids, all of which, like the sulphuric, are strongly attractive of water. But in this explanation the following circumstances were overlooked; namely, first, that water may be abstracted from alcohol by the alkalis, or by chloride of calcium, or by passing it through a red-hot tube, and yet nothing like ether is the result; secondly, that water passes over during the whole of the process along with the ether, with which the acid ought to combine, in preference to decomposing or dehydrating the alcohol; thirdly, that ether is not produced by the action of anhydrous sulphuric acid on alcohol; and, fourthly, that ether is never produced except by the aid of heat.

Mitscherlich considers the formation of ether as a case of *decomposition by contact*, conceiving that, at a certain temperature, (regulated by the dilution of the acid,) alcohol, on merely coming into the contact of sulphuric acid, is resolved into ether and water: he cites the decomposition of oxygenated water, by gold, silver, and peroxide of manganese, and the action of spongy platinum in determining the combination of certain gases, together with the conversion of sugar into alcohol and carbonic acid by the *contact* of ferment, and of starch into sugar, by means of sulphuric acid, as parallel cases. (*Ann. Ch. et Ph.*, lvi. 433; *Poggend. Annalen*, xxxi. 273.)

That the mere *abstraction of water* from the alcohol by the sulphuric acid, either in consequence of its affinity, or by contact, is not the sole or efficient cause of the formation of ether, was shown, first by Dabit (*Ann. de Chim.*, xxxiv. 289), afterwards by Sertuerner and Vogel, and subsequently by Hennell. (*Phil. Trans.*, 1826 and 1828.) Sertuerner found that the sulphuric acid underwent more complicated changes; and he called the new acid, which he conceived to result from these changes, *Enothionic acid*. Vogel afterwards found, that by the action of the alcohol, the sulphuric acid lost much of its power of precipitating the soluble salts of lead; and he called the acid into which it was converted, *Sulphovinic acid*, which term we still retain. Hennell's experiments prove, that the mutual action of the sulphuric acid and alcohol is *immediate* upon mixture; that its saturating power is diminished; that the new acid forms soluble salts with baryta, and oxide of lead, and other distinct combinations\*; he then goes on to show that this acid, the sul-

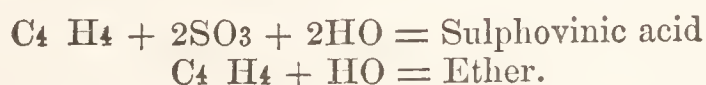
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\* The *immediate change* in the sulphuric acid is rendered evident by the following experiments: 440 grains of sulphuric acid were mixed with an equal weight of alcohol, specific gravity .820; the mixture when cold, was diluted with water, and saturated by carbonate of soda, of which it required only 398 grains; whereas 440 grains of sulphuric acid saturated 555 grains of the same carbonate: here, therefore, two-

*phovinic*, contains sulphuric acid and quadrihydrocarbon, or etherine; and considers it as the agent by which etherine is first formed, and then so evolved, as to unite with water to form ether: in short, that in the conversion of alcohol into ether, the formation of *sulphovinic acid* is an intermediate and a necessary step, and that this acid is a *bisulphate of etherine*,  $= C_4 H_4 + 2SO_3$ .

Liebig admits that the formation of sulphovinic acid is an essential step in the process of etherification, but he takes a different view of the nature of that acid, and considers it as a compound of 2 atoms of anhydrous sulphuric acid, 2 of water, and 1 of etherine; or, assuming alcohol to be a *binhydrate of etherine*, and its equivalent 46, he regards sulphovinic acid as a *bisulphate of alcohol*. Adopting this theory, it is assumed that the *formation* of sulphovinic acid is the consequence of the mutual action of alcohol and sulphuric acid upon each other, at a *given temperature*, which temperature is ensured by the state of dilution of the mixture of sulphuric acid, alcohol, and water: if the acid be too dilute, the temperature at which the mixture boils is not high enough to form the sulphovinic acid, and alcohol passes over unchanged; if it be too concentrated, the temperature is too high, and the ether is decomposed, and olefiant gas is formed; it is between these extremes that the formation of sulphovinic acid ensues; and the mixture most favorable to it, as appears from Mitscherlich's statement (p. 1667), consists of 100 parts of common sulphuric acid, 20 of water, and 50 of anhydrous alcohol.

Now, these proportions are very nearly equivalent to 2 atoms of common or hydrated sulphuric acid, 2 of water, and 1 of alcohol; or, if we represent alcohol as a *binhydrate of etherine* (see p. 1675), to 2 atoms of *anhydrous* sulphuric acid  $= 80$ , 4 of water  $= 36$ , and 1 of alcohol  $= 46$ ; and are, in themselves, such as contain the elements of *sulphovinic acid*; so that we need only suppose them to be subjected to the proper temperature for that purpose; and not only is such *temperature* obtained by Mitscherlich's method of proceeding, but it is kept up during the experiment, and, at the same time, the continuous supply of alcohol furnishes materials for the constant formation of sulphovinic acid; and the sulphovinic acid (containing 2 atoms of anhydrous sulphuric acid, and 1 of alcohol,) is no sooner formed, than it is resolved into sulphuric acid, ether, and water; ether being formed by subtracting 2 atoms of anhydrous sulphuric acid and 1 atom of water from 1 atom of sulphovinic acid, or



sevenths of the acid seem to have been saturated by, or to have entered into some new combination with, the alcohol.

440 grains of sulphuric acid were mixed, as before, with its weight of alcohol, and the mixture poured into a solution of acetate of lead; 542 grains of sulphate of lead only were precipitated; whereas the same quantity of sulphuric acid not acted upon by alcohol, threw down 1313 grains of sulphate of lead, so that four-sevenths of the acid had

lost its power of precipitating oxide of lead. Vogel and Gay-Lussac have attributed this loss of saturating power to the formation of hyposulphuric acid; and they regard the hyposulphates and sulphovinates as only differing in the latter containing ethereal oil, which in some way acts the part of water of crystallization. But that this is not a correct view of the phenomena will appear when the composition of oil of wine, and of sulphovinic acid is examined.



It now only remains briefly to recapitulate the above statements, respecting the ultimate, and the proximate or theoretical composition of alcohol and ether, in order to see their mutual bearings: and for this purpose I have represented them in the following table. It must, however, be allowed that there are many points connected with the phenomena of etherification which are not adequately explained by any of the accepted theories; some of these are well discussed and illustrated in an Essay on the mutual action of chloride of zinc and alcohol by M. Masson. (*Ann. Ch. et Ph.*, LXIX. 225.)

ALCOHOL.

|           |       | Equivalent |          |           |       | Eqvt.  |          |
|-----------|-------|------------|----------|-----------|-------|--------|----------|
|           |       | Atoms.     | Weights. |           |       | Atoms. | Weights. |
| Carbon    | ..... | 4          | .... 24  | Carbon    | ..... | 4      | .... 24  |
| Hydrogen  | ..... | 6          | .... 6   | Hydrogen  | ....  | 2      | .... 4   |
| Oxygen    | ..... | 2          | .... 16  | Do.       | ..... | 2      | .... 2   |
|           |       |            |          | Oxygen    | ..... | 2      | .... 16  |
|           |       |            |          |           |       |        |          |
| A Alcohol | ..... | 1          | 46       | B Alcohol | ..... | 1      | 46       |

ETHER.

|          |       | Atoms. |       | Equivalent Weights. |  |
|----------|-------|--------|-------|---------------------|--|
| Carbon   | ..... | 4      | ..... | 24                  |  |
| Hydrogen | ..... | 5      | ..... | 5                   |  |
| Oxygen   | ..... | 1      | ..... | 8                   |  |
| <hr/>    |       |        |       |                     |  |
| c Ether  | ..... | 1      |       | 37                  |  |
| <hr/>    |       |        |       |                     |  |

|          |       | Equivalent Atoms. |      | Equivalent Weights. |   |              |       | Equivalent Atoms. |      | Equivalent Weights. |       |      |    |      |    |
|----------|-------|-------------------|------|---------------------|---|--------------|-------|-------------------|------|---------------------|-------|------|----|------|----|
| Carbon   | ....  | 4                 | .... | 24                  | } | Olefiant gas | 2     | ....              | 28   | Etherine            | 1     | .... | 28 |      |    |
| Hydrogen | ....  | 4                 | .... | 4                   |   |              |       |                   |      |                     |       |      |    |      |    |
| Do.      | ..... | 1                 | .... | 1                   | } | Water        | ..... | 1                 | .... | 9                   | Water | .... | 1  | .... | 9  |
| Oxygen   | ....  | 1                 | .... | 8                   |   |              |       |                   |      |                     |       |      |    |      |    |
| <hr/>    |       |                   |      |                     |   |              |       |                   |      |                     |       |      |    |      |    |
| d Ether  | ....  | 1                 |      | 37                  |   | Ether        | ..... | 1                 |      | 37                  | Ether | .... | 1  |      | 37 |
| <hr/>    |       |                   |      |                     |   |              |       |                   |      |                     |       |      |    |      |    |

ETHER.

ALCOHOL.

| Eqvt.           |     |   |     | Eqvt.           |          |     |     | Eqvt.           |          |           |     | Eqvt.           |     |         |         |     |     |   |    |
|-----------------|-----|---|-----|-----------------|----------|-----|-----|-----------------|----------|-----------|-----|-----------------|-----|---------|---------|-----|-----|---|----|
| Atoms. Weights. |     |   |     | Atoms. Weights. |          |     |     | Atoms. Weights. |          |           |     | Atoms. Weights. |     |         |         |     |     |   |    |
| Carbon          | ... | 4 | ... | 24              | } Ethyle | 1   | ... | 29              | Carbon   | ...       | 4   | ...             | 24  | } Ether | 1       | ... | 37  |   |    |
| Hydrogen        | ... | 5 | ... | 5               |          |     |     |                 | Hydrogen | ...       | 5   | ...             | 5   |         |         |     |     |   |    |
|                 |     |   |     |                 |          |     |     |                 | Oxygen   | ...       | 1   | ...             | 8   |         |         |     |     |   |    |
| Oxygen          | ... | 1 | ... | 8               | Oxygen   | ... | 1   | ...             | 8        | Do.       | ... | 1               | ... | 8       | } Water | 1   | ... | 9 |    |
|                 |     |   |     |                 |          |     |     |                 | Hydrogen | ...       | 1   | ...             | 1   |         |         |     |     |   |    |
| E Ether         | ... | 1 |     | 37              | Ether    | ... | 1   |                 | 37       | F Alcohol | ... | 1               |     | 46      | Alcohol | ... | 1   |   | 46 |

A shows the ultimate elements of *alcohol*; B represents alcohol as a *binhydrate of etherine*; C shows the ultimate elements and equivalent of *ether*; D represents it as a *dihydrate of olefiant gas*, or as a *hydrate of etherine*; E exhibits ether as an *oxide of ethyle*; and F alcohol as a *hydrated oxide of ethyle*, or a *hydrate of ether*.

COMBINATIONS OF ETHER, AND OF ETHERINE OR QUADRIHYDROCARBON, WITH THE OXY-ACIDS.

OIL OF WINE. HEAVY OIL OF WINE. SULPHATIC ETHER. SULPHATE OF HYDROCARBON. SULPHATE OF ETHERYLE. When the distillation of a mixture of sulphuric acid and alcohol is carried beyond the

point at which ether ceases to come over, a portion of a liquid, looking like oil, is obtained, to which the above names have been applied; when washed, it has a bitter aromatic flavor. It has long been known under the name of *oil of wine*, and was formerly regarded as analogous in composition to the volatile oils. In endeavouring to determine the ultimate elements of this oil, by passing it over red-hot oxide of copper, Hennell always obtained *sulphurous acid*, and a solution of sulphate of copper on washing the oxide he had used, notwithstanding every precaution had been taken to free the oil from all adhering acid. A few drops of the oil were added to a solution of chloride of barium, and gently heated, but no cloud was produced, although litmus paper indicated the presence of free acid; on evaporating the mixture, however, a precipitate fell as it became concentrated; and, on boiling to dryness, sulphate of baryta was found in the residue. It appeared, therefore, that the sulphuric acid was in some state of combination which prevented its usual action upon tests; or that its elements were in some peculiar state of arrangement in the oil of wine. Hennell made some experiments to determine the quantity of sulphuric acid thus elicited, from which it appeared, that 100 grains of the oil of wine afforded about 38 grains of *sulphuric acid*. His previous experiments had shown that *hydrogen* and *carbon* were also elements of oil of wine; and, having determined their proportions by distillation through oxide of copper (adhering moisture and acid having been removed from the oil of wine by quicklime), he obtained from 100 grains (mean of several experiments) 8.30 hydrogen and 53.70 carbon; which appeared to indicate the composition of oil of wine to be 62 *hydrocarbon* + 38 *sulphuric acid*. It will be observed, that, as respects the carbon and hydrogen, the relative weights nearly approximate to 6 and 1. Hennell observes, however, in regard to the above experiments, that we can only infer from them the composition of the *hydrocarbon combined with and neutralizing the sulphuric acid*; for that oil of wine dissolves a variable quantity of hydrocarbon, part of which separates in a crystalline form when the oil is kept for some time, or when exposed to cold. Having thus far determined the composition of oil of wine, its action upon heated solutions of chloride of barium, and chloride of potassium, was more particularly examined; it having been already observed, that in those cases an *acid* is evolved, which does not precipitate baryta. Two hundred grains of oil of wine were gently heated with 6 ounces of water for an hour; precipitated carbonate of baryta was then added, which dissolved, with effervescence, to the amount of 90 grains: the solution, filtered and set to evaporate, became acid, and deposited sulphate of baryta. The experiment, therefore, was repeated; but instead of *evaporating* the barytic solution, it was precipitated by carbonate of potassa, and filtered. The filtered solution, evaporated at a temperature not exceeding 150°, remained *neutral*, and afforded lamellar crystals, greasy to the touch, very soluble in water and alcohol, burning, when heated, with a flame like that of ether, and leaving an acid sulphate of potassa. To determine the composition of the crystals, 20 grains were heated to redness, and left a residue of 10.56 grains of sulphate of potassa, equal to 4.8 sulphuric acid, and 5.76 potassa. 20 grains were dissolved in a solution of caustic potassa, boiled to dryness, heated red-hot, and, when cold, dissolved in distilled water; the excess of potassa was then saturated by nitric acid, and the solution added to



one of chloride of barium; 28 grains of sulphate of baryta were obtained, nearly equal to 9·6 of sulphuric acid; the salt, therefore, contained *twice* the quantity of sulphuric acid required to form a neutral salt with the potassa, or *two equivalents*. The remaining elements of the salt were determined by heating it with oxide of copper, from which it appeared that the components of 100 grains are, potassa 28·84, sulphuric acid 48·84, carbon 13·98, hydrogen 2·34, water 7. These numbers may be considered as indicating :—

|                                       |   |       |
|---------------------------------------|---|-------|
| 1 equivalent of potassa .....         | = | 48    |
| 2       ,,       sulphuric acid ..... | = | 80    |
| 4       ,,       carbon.....          | = | 24    |
| 4       ,,       hydrogen .....       | = | 4     |
|                                       |   | <hr/> |
|                                       |   | 156   |

Hennell proceeds to show that the salts obtained from oil of wine are identical with the *sulphovinates* procured from the mixture of sulphuric acid and alcohol; the *sulphovinic acid*, therefore, must be regarded as a compound of 2 atoms of sulphuric acid, and 1 of hydrocarbon, (consisting of 4 atoms of carbon = 24, and 4 hydrogen = 4,) and corresponding, therefore, to the *quadrihydrocarbon* or *etherine*, above described (p. 485). This acid, however, has the property of neutralizing *single* equivalents only of bases; so that *one* equivalent of the sulphuric acid appears to be neutralized by the hydrocarbon, furnishing an analogous instance to the *sulphonaphthalic acid* already mentioned (p. 491).

When *sulphovinates* are formed through the medium of *oil of wine*, a portion of quadrihydrocarbon is thrown off, amounting to half that which is contained in the oil; now, as oil of wine is a perfectly neutral compound, it may, in fact, be regarded as a *sulphovinate of etherine*, in which the etherine performs the part of a base; and we may regard it as composed of

|                      |   |        |                |       |
|----------------------|---|--------|----------------|-------|
| Sulphuric acid ..... | 2 | 80     | 2              | 80    |
| Carbon.....          | 8 | 48     | } Etherine ... | 2     |
| Hydrogen .....       | 8 | 8      |                |       |
| <hr/>                |   | <hr/>  | <hr/>          | <hr/> |
| Oil of wine .....    | 1 | 136 or | 1              | 136   |

Such is Hennell's view of the nature of *oil of wine*, and it obviously also includes that of *sulphovinic acid*, which he considers as a compound of sulphuric acid, with half the above quantity of hydrocarbon, or —

|                       |   |       |                |       |
|-----------------------|---|-------|----------------|-------|
| Sulphuric acid .....  | 2 | 80    | 2              | 80    |
| Carbon.....           | 4 | 24    | } Etherine ... | 1     |
| Hydrogen .....        | 4 | 4     |                |       |
| <hr/>                 |   | <hr/> | <hr/>          | <hr/> |
| Sulphovinic acid..... | 1 | 108   | 1              | 108   |

Or, if oil of wine be regarded as a *sulphate of etherine*, (C<sub>4</sub> H<sub>4</sub> + SO<sub>3</sub>), sulphovinic acid will be the *bisulphate* of the same base, or (C<sub>4</sub> H<sub>4</sub> + 2SO<sub>3</sub>.)

The part which the sulphovinic acid performs in the generation of ether has been already noticed, and Hennell has shown, in the papers

which I have quoted, not only that *ether* may be obtained from the sulphovinic acid as it exists in the sulphovimates, by combining its hydrocarbon with water, but also that, by doubling the water, it yields *alcohol*.

Serullas prepares *oil of wine* as follows. (*Ann. de Ch. et Ph.*, xxxix. 153.) He distils a mixture of 1 part of alcohol, and 2·5 of concentrated sulphuric acid; a little ether is first formed, then a yellow oil, accompanied by an aqueous acid liquor; the oil is separated, washed in cold water, and then transferred to the receiver of the air pump, where it is placed by two capsules, the one containing sulphuric acid, the other fragments of potassa; in this way it gradually loses the sulphurous acid, water, alcohol, and ether, with which it was mixed in its original state. It then varies much in color, becoming green and blue whilst in vacuo, but yellow when exposed to air; it has a penetrating aromatic odor, and a cooling bitterish taste; it is soluble in alcohol and ether, but not in water; its specific gravity is 1·133.

On referring, however, to the analyses of this oil, as given by Serullas, Liebig, and Dumas, it evidently differs in composition from that examined by Hennell; Dumas, indeed, states that it was not obtained twice alike, but he presumes that it contains a true sulphate of oxide of ethyle, or *sulphatic ether*\*, which, he says, should contain:—

|                                  |     |       |    |       |       | Dumas.     |
|----------------------------------|-----|-------|----|-------|-------|------------|
| Sulphuric acid.....              | 1   | ..... | 40 | ..... | 51·9  | ..... 51·6 |
| Carbon.....                      | 4   | ..... | 24 | ..... | 31·2  | ..... 31·5 |
| Hydrogen .....                   | 5   | ..... | 5  | ..... | 6·5   | ..... 6·8  |
| Oxygen .....                     | 1   | ..... | 8  | ..... | 10·4  | ..... 10·1 |
| <hr/>                            |     |       |    |       |       |            |
| Heavy oil of wine, or, sulphatic | } 1 |       |    |       | 100·0 | 100·0      |
| ether .....                      |     |       |    |       |       |            |
|                                  |     |       | 77 |       |       |            |

Oil of wine therefore is here represented as  $C_4 H_4 + SO_3 + HO$ , or as a *hydrated* sulphate, instead of an anhydrous sulphate of etherine; that is, as Hennell's oil of wine, *plus* water.

The other characters of this oil are stated to be as follows: boiled with water, it is gradually converted into sulphovinic acid and alcohol, and an *oily hydrocarbon, lighter than water*; when the boiling is long continued, the whole of the sulphovinic acid is destroyed, and sulphuric acid, alcohol, and the light oil, are the products. Heated with alkaline solutions, the heavy oil of wine is converted into sulphovinate; and the light oil, and probably alcohol, are given off. Potassium is not acted upon by it without heat, when sulphuret of potassium, and sulphate of potassa are formed.

**LIGHT OIL OF WINE. ETHEROLE.**—This, which is given off from the heavy oil in the above-mentioned processes, has a specific gravity=0·917 to 0·920; it resembles olive oil. When shaken with water, and exposed in a cold place, it gradually deposits a crystallized substance, which, dried upon blotting paper, is tasteless, friable, of an aromatic odor when heated,

\* Dumas observes that it should properly be termed *sulphuric ether*, but to avoid the confusion that would arise in consequence of the application of that term to *ether*, he modifies it as above.



specific gravity = .980, fusible at about  $230^{\circ}$  ( $110^{\circ}$  Cent.), and volatile at  $500^{\circ}$  ( $260^{\circ}$  Cent.).

There can be little doubt that this is the hydrocarbon of oil of wine, above analyzed by Hennell, and which Serullas also found composed of hydrogen and carbon in the ratio of 1 to 6.

**SULPHOVINIC ACID.**  $[C_4 H_4 + 2SO_3] + 2HO$ ; or  $HO + C_4 H_5 O + 2SO_3 = HO, AeO, 2SO_3$ .—The composition, production, and some of the properties of this acid, have been necessarily included in the account of *ether*, and from the preceding statement, founded on Hennell's researches, it may be represented in its *anhydrous* state, as a compound of 2 atoms of sulphuric acid, and 1 of etherine.

*Hydrated sulphovinic acid* may be obtained by decomposing *sulphovinate of lead* or of *baryta* by sulphuric acid, or the former by sulphuretted hydrogen; it may be concentrated by the usual process in vacuo, taking care to avoid the production of sulphuric acid. In this state it is a colorless, sour liquid, specific gravity = 1.319; it is decomposed by a gentle heat; it dissolves in all proportions in water and alcohol, but is not soluble in ether. Chlorine is apparently without action upon it, but nitric acid soon produces sulphuric acid in it. Boiled with water it yields sulphuric acid and alcohol. *Hydrated sulphovinic acid* (containing 1 atom of anhydrous acid = 108 + 2 atoms of water = 18) appears to be formed by the action of 4 atoms of protohydrated, or common liquid sulphuric acid, upon 1 atom of alcohol, in such a way that 2 atoms of anhydrous sulphuric acid unite to the elements of the alcohol, whilst the remaining 2 atoms of sulphuric acid become bihydrated. Thus we have  $4[SO_3, HO] + C_4 H_6 O_2$ , producing  $2[SO_3] C_4 H_6 O_2 + 2[SO_3, 2HO]$ . Here again hydrated sulphovinic acid presents itself as a *sulphate of alcohol*, or as a compound of 2 atoms of sulphuric acid, 1 of quadrihydrocarbon, and 2 of water. These statements are therefore as follows:—

|                           |   |     |     |       |  |       |
|---------------------------|---|-----|-----|-------|--|-------|
| Sulphuric acid .....      | 2 | ... | 80  | } = { | 1 atom anhydrous<br>sulphovinic acid...108<br>2 atoms water ..... 18 | } 126 |
| Carbon .....              | 4 | ... | 24  |       |  |       |
| Hydrogen .....            | 6 | ... | 6   |       |  |       |
| Oxygen .....              | 2 | ... | 18  |       |  |       |
| <hr/>                     |   |     |     | <hr/> |  |       |
| Hydrated sulphovinic acid | 1 |     | 126 |       |  |       |

Or,

|                                |   |     |     |            |         |     |     |           |       |     |    |     |  |  |  |
|--------------------------------|---|-----|-----|------------|---------|-----|-----|-----------|-------|-----|----|-----|--|--|--|
| Sulphuric acid                 | 2 | ... | 80  | .....      | 2       | ... | 80  | .....     | 2     | ... | 80 |     |  |  |  |
| Carbon                         | 4 | ... | 24  | } Etherine | 1       | ... | 28  | } Alcohol | 1     | ... | 46 |     |  |  |  |
| Hydrogen                       | 4 | ... | 4   |            | } Water | 2   | ... |           | 16    |     |    |     |  |  |  |
| Do.                            | 2 | ... | 2   |            |         |     |     |           |       |     |    |     |  |  |  |
| Oxygen                         | 2 | ... | 16  |            |         |     |     |           |       |     |    |     |  |  |  |
| <hr/>                          |   |     |     | <hr/>      |         |     |     |           | <hr/> |     |    |     |  |  |  |
| Hydrated sulpho-<br>vinic acid | } | 1   | 126 |            |         | 1   | 126 |           |       |     | 1  | 126 |  |  |  |
|                                |   |     |     |            |         |     |     |           |       |     |    |     |  |  |  |

The relations between the composition of oil of wine, sulphovinic acid, ether, and alcohol, are sometimes represented as follows:—

|                        |                   |
|------------------------|-------------------|
| Etherine .....         | $C_4 H_4$         |
| Oil of wine .....      | $C_4 H_4 + SO_3$  |
| Sulphovinic acid ..... | $C_4 H_4 + 2SO_3$ |
| Ether .....            | $C_4 H_4 + HO$    |
| Alcohol .....          | $C_4 H_4 + 2HO$   |

If we regard sulphovinic acid as  $\text{HIO}, \text{AeO}, 2\text{SO}_3$ , its components will be

|               |   |     |     |     |        |   |               |   |     |    |        |       |
|---------------|---|-----|-----|-----|--------|---|---------------|---|-----|----|--------|-------|
| Ethyle.....   | 1 | ... | 29  | ... | 23·01  | } | Ether .....   | 1 | ... | 37 | ...    | 29·36 |
| Oxygen .....  | 1 | ... | 8   | ... | 6·35   |   | Water.....    | 1 | ... | 9  | ...    | 7·15  |
| Water.....    | 1 | ... | 9   | ... | 7·25   |   | Sulphuricacid | 2 | ... | 80 | ...    | 63·49 |
| Sulphuricacid | 2 | ... | 80  | ... | 63·49  |   |               |   |     |    |        |       |
| <hr/>         |   |     |     |     |        |   |               |   |     |    |        |       |
| Sulphovinic   | } | 1   | 126 |     | 100·00 |   | 1             |   | 126 |    | 100·00 |       |
| acid .....    |   |     |     |     |        |   |               |   |     |    |        |       |

*Sulphovicates.* We are indebted for the first accurate analysis of these curious salts to Hennell; they are soluble in water, and many of them in alcohol, by which they are separable from their corresponding sulphates. When heated they are decomposed with varying phenomena, dependent upon the temperature to which they are submitted, and the nature of the base. At a high temperature they burn, and leave a carbonaceous residue, containing a bisulphate, or a mixture of a sulphate and sulphuric acid. Only a few of the sulphovicates have been minutely described, but they are an interesting class of salts, and some of them highly deserving further examination: the *sulphovicate of ammonia* especially deserves to be studied.

The *sulphovicates* are generally obtained by heating a mixture of equal weights of alcohol and sulphuric acid, and when cold, diluting and saturating it with carbonate of lime, baryta, or lead, when soluble sulphovicates, and insoluble sulphates of those bases are formed, and may be separated by filtration and crystallization. From these salts the other sulphovicates may be obtained, either by double decomposition, or by liberating the sulphovinic acid by sulphuric acid, and then saturating with the required bases.

*Sulphovicate of Ammonia.*  $\text{NH}_4 \text{O}, \text{AeO}, 2\text{SO}_3$ . This salt has been examined by Marchand: it forms transparent crystals soluble in water, alcohol, and ether. They fuse without loss of weight, at  $144^\circ$ . At about  $225^\circ$  their decomposition commences with the evolution of alcohol. Marchand has also described a double salt formed by the union of 1 atom of sulphovicate of ammonia with 2 of sulphovicate of potassa.

*Sulphovicate of Potassa.*  $\text{KO}, \text{AeO}, 2\text{SO}_3$ . This salt, which has already been adverted to, forms micaceous crystals, somewhat like those of hydrated boracic acid; of a greasy feel and sweetish-bitter taste. It is very soluble in water, but insoluble in ether and in alcohol. Heated to a little above  $212^\circ$ , it begins to be decomposed. Its components are—

|   |   |     |     |     |       |
|---|---|-----|-----|-----|-------|
| Potassa .....                             | 1 | ... | 48  | ... | 29·1  |
| Sulphuric acid .....                      | 2 | ... | 80  | ... | 48·5  |
| Etherine .....                            | 1 | ... | 28  | ... | 17·0  |
| Water.....                                | 1 | ... | 9   | ... | 5·4   |
| <hr/>                                     |   |     |     |     |       |
| Crystallized sulphovicate of potassa..... | 1 |     | 165 |     | 100·0 |

The most convenient representation of the composition of this salt and of the other sulphovicates is, perhaps, as follows, in accordance with the formula above given:—



|                              |   |       |     |       |        | Marchand.   |
|------------------------------|---|-------|-----|-------|--------|-------------|
| Potassa .....                | 1 | ..... | 48  | ..... | 29·09  | ..... 28·63 |
| Ether .....                  | 1 | ..... | 37  | ..... | 22·42  | ..... 22·72 |
| Sulphuric acid .....         | 2 | ..... | 80  | ..... | 48·49  | ..... 48·65 |
| <hr/>                        |   |       |     |       |        |             |
| Sulphovinate of potassa .... | 1 |       | 165 |       | 100·00 | 100·00      |

*Sulphovinate of Soda*,  $\text{NaO}, \text{AeO}, 2\text{SO}_3, + 2\text{HO}$ , yields efflorescent crystals of a bitter taste, soluble in 2 parts of cold and 1 of boiling water. In vacuo it loses its water of crystallization. Heated to about  $186^\circ$  it fuses and loses water, and then the dry salt decomposes at about  $220^\circ$ . It is soluble in alcohol, and crystallizes out of its hot alcoholic solution, in combination with alcohol, which may be abstracted by ether, in which the salt is insoluble. (MARCHAND.)

*Sulphovinate of Lithia*,  $\text{LO}, \text{AeO}, 2\text{SO}_3 + 2\text{HO}$ , may be obtained by evaporation in vacuo, in large transparent deliquescent crystals, soluble in alcohol, but insoluble in ether. (MARCHAND.)

*Sulphovinate of Lime*.  $\text{CaO}, \text{AeO}, 2\text{SO}_3 + 2\text{HO}$ . By slow evaporation this salt forms quadrilateral tables, very soluble in water and in alcohol, and of a slightly sweet taste; by desiccation in vacuo they lose 2 atoms of water: when cautiously distilled at a temperature not exceeding  $230^\circ$ , this salt yields ether.

*Sulphovinate of Baryta*,  $\text{BaO}, \text{AeO}, 2\text{SO}_3, + 2\text{HO}$ , forms permanent square tabular crystals, readily soluble in water, but insoluble in alcohol. When this salt is dried in vacuo over sulphuric acid, or at a temperature of  $130^\circ$ , it loses its water of crystallization. The components of crystallized sulphovinate of baryta may be represented as

|                                     |   |     |     |     |        | Marchand.  |
|-------------------------------------|---|-----|-----|-----|--------|------------|
| Baryta .....                        | 1 | ... | 77  | ... | 36·32  | ... 36·08  |
| Ether .....                         | 1 | ... | 37  | ... | 17·46  | ... 17·65  |
| Sulphuric acid.....                 | 2 | ... | 80  | ... | 37·73  | ... 37·79  |
| Water .....                         | 2 | ... | 18  | ... | 8·49   | ... 8·48   |
| <hr/>                               |   |     |     |     |        |            |
| Crystallized sulphovinate of baryta | 1 | ... | 212 | ... | 100·00 | ... 100·00 |

*Sulphovinate of Strontia*.  $\text{SrO}, \text{AeO}, 2\text{SO}_3$ . This salt forms large anhydrous crystals: when their dilute aqueous solution is boiled, alcohol evaporates, and sulphate of strontia is formed.

*Sulphovinate of Magnesia*,  $\text{MgO}, \text{AeO}, 2\text{SO}_3, + 4\text{HO}$ , crystallizes in square tables and in quadrangular prisms, soluble in water, but insoluble in alcohol and in ether, and efflorescent in the air. At  $175^\circ$  they lose half their water of crystallization: in vacuo over sulphuric acid, and also when boiled in alcohol, they become anhydrous. (MARCHAND.)

*Sulphovinate of Lead*.  $\text{PbO}, \text{AeO}, 2\text{SO}_3 + 2\text{HO}$ . When this salt is obtained by digesting carbonate of lead in a solution of sulphovinic acid, it yields large tabular crystals, soluble in water and in alcohol, but not in ether. It begins to be decomposed at  $175^\circ$ , but it is very unstable, and even liable to spontaneous decomposition. When digested with hydrated oxide of lead, an uncrystallizable *basic* salt is formed  $= 2\text{PbO}, \text{AeO}, 2\text{SO}_3$ , which, when heated, yields alcohol and oil of wine. (MARCHAND.)

*Sulphovinate of Copper*,  $\text{CuO}, \text{AeO}, 2\text{SO}_3 + 4\text{HO}$ , formed by dissolving carbonate of copper in sulphovinic acid, yields large blue

tabular crystals, very soluble in water and alcohol, but insoluble in ether. The aqueous solution of this salt is not precipitated by chloride of barium. When heated a little above  $212^{\circ}$ , as when long boiled in water, it passes into sulphate of copper. This salt is easily formed by adding a solution of sulphate of copper to sulphovinate of baryta.

*Sulphovinate of Silver*,  $\text{AgO}, \text{AeO}, 2\text{SO}_3, + 2\text{HO}$ . This salt forms small brilliant crystals, having, according to Marchand, the above formula: they cannot be rendered anhydrous without decomposition.

**ETHIONIC ACID. ETHEROSULPHURIC ACID.** When the vapor of anhydrous sulphuric acid is slowly introduced into absolute alcohol, kept at a low temperature, an oleaginous liquid is formed, and no gas evolved: if too little alcohol has been used, crystals of sulphuric acid form, which redissolve when alcohol is added. The liquid when mixed with water does not heat, and on saturating the solution with baryta, abundance of sulphate of baryta is formed, together with a soluble salt of baryta, which must be evaporated *in vacuo*. This salt contains sulphuric acid, but it is not sulphovinate of baryta, for it is neither soluble in alcohol nor crystallizable; nor does it yield oil of wine when distilled. It contains, according to Magnus (*Ann. Ch. et Ph.*, liii. 155),

|                           |   |       |     |       |       |
|---------------------------|---|-------|-----|-------|-------|
| Sulphuric acid.....       | 2 | ..... | 80  | ..... | 41.2  |
| Baryta.....               | 1 | ..... | 77  | ..... | 39.7  |
| Carbon.....               | 4 | ..... | 24  | ..... | 12.4  |
| Hydrogen .....            | 4 | ..... | 4   | ..... | 2.1   |
| Water .....               | 1 | ..... | 9   | ..... | 4.6   |
| <hr/>                     |   |       |     |       |       |
| Ethionate of baryta ..... | 1 |       | 194 |       | 100.0 |

According to Magnus, the acid contained in this salt is constituted of

|                     |   |       |     |       |       |
|---------------------|---|-------|-----|-------|-------|
| Sulphuric acid..... | 2 | ..... | 80  | ..... | 68.4  |
| Etherine .....      | 1 | ..... | 28  | ..... | 23.9  |
| Water .....         | 1 | ..... | 9   | ..... | 7.7   |
| <hr/>               |   |       |     |       |       |
| Ethionic acid ..... | 1 |       | 117 |       | 100.0 |

So that it is, in fact,  $= \text{AeO}, 2\text{SO}_3$ ; that is, an *anhydrous bisulphate of ether*; or sulphovinic acid, *minus* an atom of water.

By partially decomposing ethionic acid by heat, Magnus obtained an isomeric acid, which has been termed *isæthionic acid*: the salt which it forms with baryta, resembles the ethionate of that base in ultimate composition, but differs from it in its properties.

According to Dumas, the existence of these distinct acids, namely, the sulphovinic, ethionic, and isæthionic, resulting from the mutual action of sulphuric acid and alcohol, was anticipated by Sertuerner, under the terms of *protethionic*, *deutethionic*, and *tritethionic* acids. (*Ann. Ch. et Ph.*, xiii. 62.) There seems, however, reason to doubt the definite character of these compounds, as distinct from the sulphovinic acid.

Two other acids of this class have been described, namely *Methionic acid*, obtained by the action of anhydrous sulphuric acid upon ether; and *Althionic acid*, found in the residue of the preparation of olefiant gas by sulphuric acid and alcohol; but the distinctive characters of these



acids have not been definitely ascertained. (REGNAULT, *Ann. Ch. et Ph.*, LXV. 98. ETTLING.)

**SULPHUROUS ETHER.** **SULPHITE OF OXIDE OF ETHYLE.**  $C_4H_5O, SO_2$ . Add alcohol to chloride of sulphur, and when all action ceases, distil the mixture; alcohol acidified by hydrochloric acid first passes over: the temperature then rises to  $302^\circ$ , and the liquid distilled between  $302^\circ$  and  $338^\circ$ , yields, on rectification, a colorless ether having the above composition. It has a peculiar mint-like odor; a hot and sulphurous taste; sp. gr. 1.085; boils at  $322^\circ$ : it is soluble in alcohol and ether, from which it is at first thrown down by water, which afterwards dissolves it and acquires the odor of sulphurous acid. The density of its vapor is 4.76. (EBELMEN and BOUQUET. *Comptes Rendus*, May, 1845.)

**ETHEROPHOSPHOROUS ACID.**  $2HO, AeO, PO_3$ . This compound was discovered by Wurtz. (*Ann. Ch. et Ph.*, 3ème Sér., xvi. 218.) It is produced by dropping terchloride of phosphorus into alcohol of sp. gr. 0.835: the results are hydrochloric acid, chloride of ethyle, and etherophosphorous acid.  $2AeO, + PCl_3, + 2HO, = 2HCl, + AeCl + AeO, PO_3$ . When the action is complete, the liquor is evaporated *in vacuo* over pieces of caustic potassa, when a syrupy compound of etherophosphorous acid, phosphorous acid, and hydrochloric acid, remains: this is saturated with carbonate of baryta, filtered from the precipitated phosphite of baryta, and evaporated *in vacuo*. The residue is then dissolved in absolute alcohol, and again evaporated *in vacuo*, when *etherophosphite of baryta* remains, in the form of a white deliquescent uncrystallizable mass, soluble in water and in alcohol, and precipitable from its alcoholic solution by means of ether. In its dry state this salt is permanent, but in aqueous solution it passes into phosphite of baryta and alcohol. It is decomposed by heat, and resolved into inflammable gas containing phosphuretted hydrogen, and phosphite of baryta with a small quantity of red oxide of phosphorus remains. The formula of this salt is  $\left. \begin{matrix} BaO \\ HO \end{matrix} \right\} AeO, PO_3$ . The *etherophosphite of lead*  $= \left. \begin{matrix} PbO \\ HO \end{matrix} \right\} AeO, PO_3$ , may be similarly obtained; it forms lamellar crystals, soluble in water and in alcohol, but insoluble in ether. The aqueous solution decomposes spontaneously.

**ETHEROPHOSPHORIC ACID.** **PHOSPHOVINIC ACID.** It was ascertained many years ago by Boullay, that phosphoric acid might be substituted for sulphuric, in the formation of ether, and Lassaigne found that an acid analogous to the sulphovinic was so formed; the further investigation of this subject has been pursued by Pelouze and by Liebig. (*Ann. Ch. et Ph.*, liii. 37, and liv. 31; and *Ann. der Pharm.*, vi. 129 and 149.)

*Etherophosphoric acid*,  $2HO, AeO, PO_5$ , is obtained by the careful decomposition of the *etherophosphate of baryta* by sulphuric acid, or of the etherophosphate of lead by sulphuretted hydrogen; it is concentrated first by ordinary evaporation, and then *in vacuo*. It is then of an oleaginous consistence, colorless, inodorous, very sour, and soluble in water, alcohol, and ether, in all proportions. When much diluted it is

not decomposed by continued boiling; but when concentrated, a temperature of  $212^{\circ}$  gradually resolves it into ether, alcohol, hydrocarbon, and a mixture of phosphoric acid and charcoal. Its concentrated solution affords crystals: it coagulates albumen; and has the same properties whether prepared from phosphoric or from paraphosphoric acid. When diluted it dissolves zinc with effervescence, and expels carbonic acid from its combinations, forming salts which for the most part are soluble. Pelouze regards this acid as analogous to the sulphovinic in its atomic composition, or as a compound of phosphoric acid and alcohol; but from Liebig's analysis it appears to consist of phosphoric acid and ether, and, therefore, resembles the ethionic acid.

*Etherophosphate of Baryta.*  $2\text{BaO}, \text{AeO}, \text{PO}_5 + 12\text{HO}$ . This salt is obtained as follows. A very concentrated aqueous solution of phosphoric acid is mixed with its weight of alcohol, and when the mixture is cool, it is diluted with 7 to 8 parts of water, saturated by carbonate of baryta, and boiled to expel alcohol; it is then filtered to separate phosphate of baryta, and the filtrate yields on evaporation colorless six-sided tables, having the above formula, but which may be rendered anhydrous by heat. This salt effloresces in the air: its solubility in water increases up to  $104^{\circ}$ , at which temperature 100 parts of water dissolve 9.36 of the salt; but at  $212^{\circ}$ , only 2.80 parts. This salt may be heated nearly to redness without decomposition.

ARSENIOVINIC ACID. ETHEROARSENIC ACID. A compound having the formula  $2\text{AeO}, + \text{As O}_5$  has been described by D'Arcet, but its properties and composition are as yet very imperfectly known.

NITROUS ETHER. HYPONITROUS ETHER. NITRITE OF OXIDE OF ETHYLE.  $\text{AeO}, \text{NO}_3$ . The production of an ethereal fluid by the mutual action of nitric acid and alcohol is said to have been remarked by Paracelsus, and afterwards by Kunckel, but it was forgotten till rediscovered by Navier, in 1742. (NAVIER and GEOFFROY, *Mém. de l'Acad. de Paris*, 1742.) It was subsequently studied by Thenard (*Mém. d'Arcueil*, i. 75, and 359,) and more recently by Dumas and Boullay. (*Ann. Ch. et Ph.*, xxxvii. 19.)

Many processes have been published for the preparation of this ether (see DUMAS, *Chim. app. aux Arts*, v. 553, and THOMSON, *Inorg. Chem.*, ii. 317); among them the following, suggested by Thenard, is the least objectionable. Introduce into a sufficiently capacious tubulated retort equal weights of alcohol (specific gravity .820) and of nitric acid of commerce (specific gravity 1.30), and connect it with five Woulfe's bottles, the first of which is empty, and the remaining four half-filled with a saturated solution of salt in water. Apply a gentle heat to the retort, till the liquor begins to effervesce; then withdraw the fire, and the vapor passing through the bottles, which should be kept cold by a mixture of ice and salt, deposits the ether upon the saline solution. In performing this experiment, the retort should not be more than one-sixth filled with the mixture of acid and alcohol; and cold water or other means should be at hand to cool it, if required, in order to subdue the violence of the effervescence. The alcohol should be first poured in,



and then the acid, and not mixed by agitation. If the materials are warm, the acid fuming, and the alcohol of proper strength, the action often begins immediately, with a cracking noise, escape of air-bubbles, and great effervescence, so that, notwithstanding the size of the retort, its contents are very apt to pass over into the first receiver, and it is often burst; this may generally be prevented by applying a wet cloth to the retort. The tubes through which the vapor is to pass should not be too small, for, in consequence of the suddenness and abundance of its extrication, it requires a ready means of escape: indeed, the whole process requires much management and caution, and is most successful when conducted upon rather a small scale in a large retort; with from 2 to 4 ounces of alcohol and acid for instance.

When the effervescence has entirely ceased, the residue in the retort is found to be equal in bulk to less than one-third of the materials employed: the first bottle contains an acid mixture of alcohol, water, and nitrous ether; but the bulk of the ethereal product is found upon the cold saline solution of the second bottle; a little also passes into the third bottle. The ethereal products are collected, digested with powdered lime, and redistilled into a receiver cooled by ice: not more than 10 parts of *rectified ether* are usually obtained from 100 of the mixture of acid and alcohol. Besides the ether, many other products are the result of this operation, such as nitrogen and its oxides, nitrous acid, carbonic acid, and traces of acetic acid and acetic ether: oxalic acid sometimes is found in the contents of the retort.

Liebig prepares nitrous ether as follows: 1 part of starch is heated in a retort with 10 parts of nitric acid, sp. gr. 1.3. The retort is connected by means of a long glass tube, with a tubulated bottle containing a mixture of 2 parts of alcohol sp. gr. 0.835, with 1 part of water, and kept cool by being wrapped in a wet cloth: the other opening of this bottle is connected by means of a tube, with a condenser, to which a receiver is attached, (*Liebig's Condenser*, as represented at p. 79.) When the nitrous acid produced in the retort passes through the diluted alcohol, it decomposes it so as to form nitrous ether vapor, which is condensed, and ultimately collected in the receiver: it is purified by being shaken with water, and is then dehydrated by chloride of calcium.

*Nitrous ether* has the following properties. It has a slightly yellow tint, and a peculiar odor, which, when much diffused, is not unlike that of ripe apples; its specific gravity is 0.880 at 40°. (0.947 at 60°, LIEBIG. 0.909, FAVRE.) It is extremely volatile, boiling under mean pressure at a temperature of about 70°, so that at summer heat it is apt, on removing the stopper of a bottle containing it, to evaporate very rapidly, and even to enter into spontaneous ebullition: dropped upon the hand it instantly disappears and excites great cold. The specific gravity of its vapor is 2.568; or experimentally, 2.627. (DUMAS and BOULLAY.) It is very inflammable, burning with a yellowish flame, and leaving no perceptible residue; when recent, it has no action on litmus, but in a few days it becomes perceptibly sour, especially in the presence of moisture and light. Mixed with water, a part is dissolved, and another part decomposed, forming nitric acid, and giving off nitrous gas; mixed with solution of potassa it soon forms hyponitrite of potassa, alcohol, and traces of acetate of potassa. It is without action on ammonia.

The ultimate components of this ether, are

|                    |   |       |    |       |        | Dumas and<br>Boullay. |
|--------------------|---|-------|----|-------|--------|-----------------------|
| Carbon .....       | 4 | ..... | 24 | ..... | 32.00  | 32.69                 |
| Hydrogen .....     | 5 | ..... | 5  | ..... | 6.67   | 6.85                  |
| Oxygen .....       | 4 | ..... | 32 | ..... | 42.67  | 41.46                 |
| Nitrogen .....     | 1 | ..... | 14 | ..... | 18.66  | 19.00                 |
| <hr/>              |   |       |    |       |        |                       |
| Nitrous ether .... | 1 |       | 75 |       | 100.00 | 100.00                |

These elements are equivalent to

|                      |   |     |    |     |       |             |       |     |     |     |       |
|----------------------|---|-----|----|-----|-------|-------------|-------|-----|-----|-----|-------|
| Ethyle .....         | 1 | ... | 29 | ... | 38.7  | } Ether.... | 1     | ... | 37  | ... | 49.4  |
| Oxygen.....          | 1 | ... | 8  | ... | 10.7  |             |       |     |     |     |       |
| Hyponitrous acid.... | 1 | ... | 38 | ... | 50.6  |             | ..... | 1   | ... | 38  | ...   |
| <hr/>                |   |     |    |     |       |             |       |     |     |     |       |
| Nitrous ether .....  | 1 |     | 75 |     | 100.0 | or          | 1     |     | 75  |     | 100.0 |

Or they may be represented by

|                     |   |     |    |     |       |                  |   |     |    |
|---------------------|---|-----|----|-----|-------|------------------|---|-----|----|
| Olefiant gas.....   | 2 | ... | 28 | ... | 37.3  | Etherine .....   | 1 | ... | 28 |
| Water.....          | 1 | ... | 9  | ... | 12.0  | or, Water .....  | 1 | ... | 9  |
| Hyponitrous acid    | 1 | ... | 38 | ... | 50.7  | Hyponitrous acid | 1 | ... | 38 |
| <hr/>               |   |     |    |     |       |                  |   |     |    |
| Nitrous ether ..... | 1 |     | 75 |     | 100.0 |                  | 1 |     | 75 |

The composition of the other ethers of this class admits of similar hypothetical representation; but the simplest view of the subject is that which regards them as *salts of the oxide of ethyle*, or *neutral combinations of ether with the acids*.

NITRIC ETHER. NITRATE OF OXIDE OF ETHYLE.  $C_4H_5O, NO_5$ .  
Millon succeeded in obtaining a true *nitrate of ether*, and preventing the formation of nitrous acid in a mixture of nitric acid and alcohol, by the addition of nitrate of urea; 1 volume of pure nitric acid sp. gr. 1.401, and 2 volumes of alcohol sp. gr. .842, (being nearly equal weights,) are mixed with a proper proportion of nitrate of urea, one or two parts of the latter sufficing for 120 to 150 parts of the mixture; the operation succeeds best upon the small scale, as upon 4 or 5 ounces of the mixture: it should be gently heated, and about seven-eighths distilled over, in which case the operation proceeds quietly, and without that violence which occurs in the absence of urea: the nitrate of urea remains nearly intact, and may be repeatedly used. The first product is weak alcohol, soon followed by the nitric ether, which is recognised by a peculiar odor, and which on the addition of a little water falls in the form of a dense liquid; it is purified by washing with an alkaline solution, then left for a day or two in contact of fragments of chloride of calcium, and distilled. (*Ann. Ch. et Ph.*, 3ème Sér., viii. 233.) Nitric ether has a peculiar sweet odor distinct from that of nitrous ether; its taste is sweet and slightly bitter; its density 1.112 at 62°; its boiling-point 185°: it decomposes at a temperature a little above this: it burns with a very white flame: it is not decomposed by caustic potassa, except in alcoholic solution, in which case crystals of nitrate of potassa without any nitrite, are formed: it is insoluble in water, but soluble in alcohol, from which a little water immediately precipitates it: it is decomposed by nitric acid,



not yielding nitrovinic acid or nitrovinates: with hydrochloric acid it forms nitrohydrochloric acid. When added by drops to sulphuric acid, it is at first dissolved, but presently nitric acid is evolved, the mixture heats, evolves nitrous gas, and leaves a black residue: with iodine it forms a blue solution: chlorine decomposes it. It is composed of

|              |   |     |    |     |       | Millon. |        |   |  |  |  |  |
|--------------|---|-----|----|-----|-------|---------|--------|---|--|--|--|--|
| Carbon.....  | 4 | ... | 24 | ... | 26.4  | ...     | 26.59  | } |  |  |  |  |
| Hydrogen     | 5 | ... | 5  | ... | 5.5   | ...     | 5.72   |   |  |  |  |  |
| Oxygen       | 6 | ... | 48 | ... | 52.7  | ...     | 52.52  |   |  |  |  |  |
| Nitrogen     | 1 | ... | 14 | ... | 15.4  | ...     | 15.26  |   |  |  |  |  |
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| Nitric ether | 1 |     | 91 |     | 100.0 |         | 100.00 |   |  |  |  |  |
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chloride of silicium and alcohol in the formation of these ethers appears to be as follows:  $\text{Si Cl}_2 + 2[\text{AcO}, \text{HO}] = 2[\text{AeO}] \text{SiO}_2 + 2\text{H Cl}$ . (EBELMEN. *Comptes Rendus*, August, 1844, and *Ann. Ch. et Ph.*, 3ème Sér., xvi. 152.)

**BORIC ETHER.** BORATE OF OXIDE OF ETHYLE.  $\text{AeO}, 2\text{BO}_3$ . This ether was discovered by Ebelmen. (*Ann. Ch. et Ph.*, 3ème Sér., xvi. 130.) When equal parts of finely pulverized fused boracic acid and alcohol are mixed, heat is evolved; on distilling this mixture till it attains the temperature of  $230^\circ$ , and then stopping the process, the residue in the retort yields, when agitated with ether, a solution which is to be gradually heated up to  $392^\circ$ ; what then remains is *boric ether*; at this temperature it exhales dense fumes, but it concretes on cooling, forming a transparent glassy substance, viscid at temperatures between  $105^\circ$  and  $120^\circ$ . It has a slight acrid taste. Upon the skin it produces irritation, and forms pulverulent boracic acid. It is soluble in ether and in alcohol. Heated to  $570^\circ$  it is resolved into olefiant gas and boracic acid. Agitated with water heat is evolved, and boracic acid and alcohol are the products. (See also BOWMAN. *Mem. Chem. Soc.*, III. 248.)

**OXALIC ETHER.** OXALATE OF OXIDE OF ETHYLE.  $\text{AeO} + \text{C}_2\text{O}_3$ . This compound was discovered by Bergmann (*Opusc. Chim. Phys.*, i.); it was afterwards examined by Thenard (*Mém. d'Arcueil*, ii. 11), and its principal properties shown by Dumas and Boullay. (*Ann. Ch. et Ph.*, xxxvii. and liv.) It is prepared, 1, by distilling 1 part of alcohol, 1 of oxalic acid, and 2 of sulphuric acid; alcohol and sulphuric ether pass over, and are followed by an oil-like liquid which collects at the bottom of the receiver, and which is *oxalic ether*: it must be separated from the supernatant liquid, and poured into a glass of water; it often floats at first, but as the sulphuric ether which it contains gradually evaporates, it falls in drops to the bottom. On adding the alcohol in the receiver, or a fresh portion of alcohol to the residuary contents of the retort, a fresh portion of oxalic ether may be obtained; and this may even be repeated a third time: the different portions of oxalic ether thus obtained are mixed, and purified by boiling with powdered litharge, till its boiling-point attains  $360^\circ$  ( $183^\circ$  or  $184^\circ$  Cent.), when it becomes stationary: performing this operation in a flask with a short neck, the water, sulphuric ether, and alcohol, pass off in vapor, and the excess of acid is retained by the oxide of lead; the oxalic ether is then decanted into a clean dry retort and redistilled. 2. According to Bauhoff and Mitscherlich a pure oxalic ether is obtained as follows: 1 part of crystallized oxalic acid and 6 parts of absolute alcohol are distilled in a tubulated retort, with an inserted thermometer, till the temperature rises to  $285^\circ$ ; 6 parts more of alcohol are then added, and distillation continued till the temperature attains  $320^\circ$ . The liquor which now remains in the retort, and which consists chiefly of oxalic ether, is shaken with water to separate free oxalic acid, and then distilled over oxide of lead. When the temperature attains  $355^\circ$ , the receiver is changed, and what then distils over is pure oxalic ether.

Oxalic ether, thus prepared, is of specific gravity  $= 1.0929$  at  $45^\circ$ : it boils at  $360^\circ$ , at mean pressure, yielding a vapor of low tension, the



density of which is 5·08: its odor is aromatic, with a slight taint of garlic or phosphorus; it is soluble in alcohol and ether, and very sparingly so in water. When dry, it may be long preserved without decomposition; but when humid, it is soon resolved into oxalic acid and alcohol; the hydrated alkalis immediately effect this change, becoming oxalates, and evolving alcohol. It consists of:—

|              |   |     |    |     |        |     |       |       |              |                       |     |    |     |       |  |  |  |  |  |  |  |
|--------------|---|-----|----|-----|--------|-----|-------|-------|--------------|-----------------------|-----|----|-----|-------|--|--|--|--|--|--|--|
|              |   |     |    |     |        |     |       |       |              | Dumas and<br>Boullay. |     |    |     |       |  |  |  |  |  |  |  |
| Carbon ..... | 6 | ... | 36 | ... | 49·31  | ... | 49·7  | } = { | Ether .....  | 1                     | ... | 37 | ... | 50·69 |  |  |  |  |  |  |  |
| Hydrogen.... | 5 | ... | 5  | ... | 6·85   | ... | 6·5   |       | Oxalic acid  | 1                     | ... | 36 | ... | 49·31 |  |  |  |  |  |  |  |
| Oxygen.....  | 4 | ... | 32 | ... | 43·84  | ... | 43·8  |       |              |                       |     |    |     |       |  |  |  |  |  |  |  |
| <hr/>        |   |     |    |     |        |     |       |       |              | <hr/>                 |     |    |     |       |  |  |  |  |  |  |  |
| Oxalic ether | 1 |     | 73 |     | 100·00 |     | 100·0 |       | Oxalic ether | 1                     |     | 73 |     | 100·0 |  |  |  |  |  |  |  |

OXAMIC ETHER. OXAMATE OF OXIDE OF ETHYLE. OXAMETHANE. When a current of dry ammoniacal gas is passed into anhydrous oxalic ether, heat is evolved, and a solid compound is at length formed, which, dissolved in boiling alcohol and filtered, yields silky crystals on cooling. The same compound may be obtained, according to Liebig (*Ann. Ch. et Ph.*, liv. 225 and lv. 125), by mixing oxalic ether with an alcoholic solution of ammonia; the mixture yields crystals on spontaneous evaporation. To the substance thus obtained, Dumas has applied the name *oxaméthane*. It is colorless, fusible, volatile, soluble in alcohol, soluble in cold water, but converted, by boiling, into acid oxalate of ammonia. Liquid ammonia immediately converts it into *oxamide*. This substance consists, according to Dumas, of 1 atom of oxalic ether, and 1 atom of ammonia; so that its ultimate elements are

|                |   |     |    |                  |    |                |    |
|----------------|---|-----|----|------------------|----|----------------|----|
| Carbon.....    | 6 | ... | 36 | } = Oxalic ether | 73 | } = Oxaméthane | 90 |
| Hydrogen ..... | 5 | ... | 5  |                  |    |                |    |
| Oxygen .....   | 4 | ... | 32 |                  |    |                |    |
| Nitrogen ..... | 1 | ... | 14 | } = Ammonia....  | 17 |                |    |
| Hydrogen ..... | 3 | ... | 3  |                  |    |                |    |

These elements are equivalent to

|                |   |     |    |                   |    |
|----------------|---|-----|----|-------------------|----|
| Carbon.....    | 2 | ... | 12 | } = Oxamide.....  | 44 |
| Hydrogen ..... | 2 | ... | 2  |                   |    |
| Oxygen .....   | 2 | ... | 16 |                   |    |
| Nitrogen ..... | 1 | ... | 14 | } = Alcohol ..... | 46 |
| Carbon .....   | 4 | ... | 24 |                   |    |
| Hydrogen ..... | 6 | ... | 6  |                   |    |
| Oxygen .....   | 2 | ... | 16 |                   |    |

Hence it is, that when aqueous ammonia and oxalic ether are mixed and agitated together, a white precipitate falls, consisting of pure *oxamide*.

Lewy has described a crystallizable compound of oxalic ether with perchloride of tin, = AeO, C2 O3, + Sn Cl2. (*Ann. Ch. et Ph.*, 3ème Sér., Mars, 1846.)

ETHEROCARBONIC ACID. AeO, HO, 2CO2. A substance having the preceding formula has been described by Dumas and Peligot (*Comptes Rendus*, vi. 1838). It has hitherto only been obtained in combination with potassa, and requires further examination. Its ultimate elements

appear, according to the above formula, to be  $\equiv \text{C}_6 \text{H}_6 \text{O}_6$ , so that its composition accords with that of *sugar*, which is known to be resolved by fermentation into carbonic acid and alcohol.

**CARBONIC ETHER. CARBONATE OF OXIDE OF ETHYLE.**  $\text{C}_4 \text{H}_5 \text{O} + \text{CO}_2$ . According to Ettling, *carbonate of oxide of ethyle* is formed during the action of potassium or sodium on oxalic ether. (*Journ. de Pharm.*, xix. 17.) The sodium is added till there is no further evolution of carbonic oxide, even on the application of a gentle heat. When the residue is treated with water, the carbonic ether separates, and, if not free from oxalic ether, it may be purified by rectification over sodium. This ether has also been obtained and examined by Cahours (*Ann. Ch. et Ph.*, Oct. 1843, p. 28); it is a limpid colorless liquid, of an ethereal odor, lighter than water, volatile without decomposition at  $258^\circ$  ( $125^\circ \text{C.}$ ) It is insoluble in water, but soluble in alcohol and in ether. The density of its vapor is 4.07. Under the influence of diffused light, chlorine so decomposes it that 2 equivalents of hydrogen are replaced by 2 of chlorine, and this compound, exposed with chlorine to direct sunshine, yields a further evolution of hydrochloric acid, and a crystalline compound. When carbonic ether is heated with potassium, it evolves (according to Löwig and Weidmann) carbonic oxide, and a mixture of ether and potassa and carbonate of potassa remains.  $\text{AeO}, \text{CO}_2 + \text{K} = \text{AeO}, \text{KO} + \text{CO}$ . A mixture of carbonic ether and aqueous ammonia yields, according to Dumas (*Comptes Rendus*, xxi. 629), a compound of carbamide with carbonic ether, and alcohol.  $2[\text{AeO}, \text{CO}_2] + \text{NH}_3 = [\text{AeO}, \text{CO}_2 + \text{NH}_2, \text{CO}] + [\text{AeO}, \text{HO}]$ .

The elements of carbonic ether are

|                |       |     |       |     |       | Ettling. |        |       |               |       |     |       |     |        |
|----------------|-------|-----|-------|-----|-------|----------|--------|-------|---------------|-------|-----|-------|-----|--------|
| Carbon.....    | 5     | ... | 30    | ... | 50.9  | ...      | 51.30  | } = { | Ether .....   | 1     | ... | 37    | ... | 62.71  |
| Hydrogen ...   | 5     | ... | 5     | ... | 8.5   | ...      | 8.58   |       | Carbonic acid | 1     | ... | 22    | ... | 37.29  |
| Oxygen .....   | 3     | ... | 24    | ... | 40.6  | ...      | 40.12  |       |               | 1     | ... | 22    | ... | 37.29  |
| <hr/>          | <hr/> |     | <hr/> |     | <hr/> |          | <hr/>  |       |               | <hr/> |     | <hr/> |     | <hr/>  |
| Carbonic ether | 1     |     | 59    |     | 100.0 |          | 100.00 |       |               | 1     |     | 59    |     | 100.00 |

**OXALOVINIC ACID.**  $\text{HIO} + \text{AeO}, 2\text{C}_2 \text{O}_3$ . When a solution of oxalic ether in anhydrous alcohol is mixed with a similar solution of potassa, in such proportion as to saturate half the acid contained in the ether, crystals are soon deposited, which are almost insoluble in absolute alcohol, and which consist of *oxalovinate of potassa*. This salt is soluble in water, and is not affected by a temperature of  $212^\circ$ ; it is anhydrous, and consists of 1 atom of oxalate of potassa, and 1 atom of oxalic ether. It may be decomposed by dissolving it in weak alcohol, filtering the solution to separate a little oxalate of potassa which falls, and then carefully adding sulphuric acid, by which sulphate of potassa is formed and precipitated, and oxalovinic acid set free. It decomposes the carbonates of lime and of baryta, and forms soluble oxalovinates; the pure acid may easily be obtained from the *oxalovinate of baryta*. Many bases, among which is the oxide of copper, decompose this acid, and produce oxalates. When its aqueous solution is evaporated, even with the utmost caution, oxalic acid remains, and the oxalovinic acid disappears. Oxalovinic acid consists of 2 atoms of oxalic acid, 1 atom of ether, and 1 of water,



which atom of water is replaced, in the oxalovينات, by an atom of base, oxalovinate of potassa being  $= \text{KO}, [\text{AeO} + 2\text{C}_2\text{O}_3]$ .

FORMIC ETHER. FORMIATE OF OXIDE OF ETHYLE.  $\text{AeO} + \text{C}_2\text{H O}_3$ . 1. Distil 7 parts of dry and pulverized *formiate of soda*, with 10 of sulphuric acid, and 6 of anhydrous alcohol; agitate the product, first with a little magnesia to separate acid, and then with water to abstract alcohol; lastly, deprive it of water, and of residuary traces of alcohol, by the action of chloride of calcium. (DÖBEREINER, *Ann. Ch. et Ph.*, lii. 105.) 2. To an intimate mixture of 10 parts of starch with 37 parts of finely pulverized black oxide of manganese, add a mixture of 30 parts of sulphuric acid with 15 of alcohol; apply heat so as to keep up gentle boiling, and distil as long as ether passes over. Dissolve chloride of calcium in the distillate to separate water and alcohol, and distil off the formic ether in a water-bath; lastly, again rectify it over chloride of calcium. (WÖHLER.)

Formic ether is colorless, and has somewhat of an hydrocyanic odor. Its specific gravity is  $= 0.915$  at  $65^\circ$ . It boils at  $132^\circ$ . The sp. gr. of its vapor is 2.58. It requires 9 parts of water at  $65^\circ$  for solution, and when boiled with water, especially if potassa be present, it is resolved into alcohol and formic acid. This ether has been analysed by Kopp (*Ann. der Pharm.*, LV. 181), according to whom it consists of

|                  |   |     |    |     | Kopp.  |     |        |       |             |   |     |    |     |     |
|------------------|---|-----|----|-----|--------|-----|--------|-------|-------------|---|-----|----|-----|-----|
| Carbon .....     | 6 | ... | 36 | ... | 48.55  | ... | 48.16  | } = { | Ether.....  | 1 | ... | 37 | ... | 50  |
| Hydrogen .....   | 6 | ... | 6  | ... | 8.11   | ... | 8.31   |       | Formic acid | 1 | ... | 37 | ... | 50  |
| Oxygen .....     | 4 | ... | 32 | ... | 43.34  | ... | 43.53  |       |             |   |     |    |     |     |
| <hr/>            |   |     |    |     | <hr/>  |     |        |       |             |   |     |    |     |     |
| Formic ether.... | 1 |     | 74 |     | 100.00 |     | 100.00 |       |             | 1 |     | 74 |     | 100 |

OXYCHLOROCARBONIC ETHER.  $\text{AeO}, \text{CO}_2, + \text{CO Cl}$ . When absolute alcohol is admitted into a balloon containing chlorocarbonic acid gas, it becomes warm and yellowish; when the action has terminated, air is admitted, and soon after, the liquid may be poured out and mixed with about its volume of distilled water; two layers are presently formed, the one of an oil-like liquid, the other lighter, and containing free hydrochloric acid. The oily liquor, abstracted by a pipette, and rectified over chloride of calcium and litharge, in a water-bath, has the following properties. It is a colorless liquid, without action on litmus; its odor is peculiar and irritating; it boils at about  $200^\circ$ ; its specific gravity  $= 1.133$  at  $60^\circ$ . It consists of

|                            |   |     |       |     |       | Dumas. |       |
|----------------------------|---|-----|-------|-----|-------|--------|-------|
| Carbon .....               | 6 | ... | 36    | ... | 33·0  | ...    | 34·2  |
| Hydrogen .....             | 5 | ... | 5     | ... | 4·6   | ...    | 5·0   |
| Oxygen .....               | 4 | ... | 32    | ... | 29·4  | ...    | 30·1  |
| Chlorine .....             | 1 | ... | 36    | ... | 33·0  | ...    | 30·7  |
| <hr/>                      |   |     | <hr/> |     | <hr/> |        | <hr/> |
| Chlorocarbonic ether ..... | 1 |     | 109   |     | 100·0 |        | 100·0 |

Dumas, from whom I have made the preceding abstract (*Chim. app. aux Arts*, v. 570; *Ann. Ch. et Ph.*, liv. 225), considers this ether as including a new acid. When it is mixed with liquid ammonia, violent action ensues, hydrochlorate of ammonia is formed, and a new product, called by Dumas *uréthan*, is formed; it is obtained by evaporating the

mixture *in vacuo* to dryness, and distilling in a dry retort, heated by an oil bath; a colorless liquid passes over, which concretes into a white crystalline matter, like spermaceti, and sal-ammoniac remains in the retort.

*Urethan* is white, fusible, and volatile when dry, without decomposition; but, when moist, ammonia is plentifully evolved; it is readily soluble in water and in alcohol, and the solution is neutral. It consists of

|                |   |     |    |     |        | Dumas. |
|----------------|---|-----|----|-----|--------|--------|
| Carbon.....    | 6 | ... | 36 | ... | 40.45  | 40.5   |
| Hydrogen ..... | 7 | ... | 7  | ... | 7.86   | 7.9    |
| Oxygen .....   | 4 | ... | 32 | ... | 35.95  | 36.0   |
| Nitrogen ..... | 1 | ... | 14 | ... | 15.74  | 15.6   |
| <hr/>          |   |     |    |     |        |        |
| Urethan .....  | 1 |     | 89 |     | 100.00 | 100.0  |

The formula assigned to this compound is  $\text{AeO}, \text{CO}_2, + \text{NH}_2, \text{CO}$ ; but it may also be represented as containing the elements of etherine, carbonic acid, water, and urea; or as  $= \text{C}_4 \text{H}_4 + \text{HO}, + \text{CO}_2, + \text{CH}_2 \text{O N}$ . It is in reference to this view that Dumas termed it *Urethan*.

ACETIC ETHER. 'ACETATE OF OXIDE OF ETHYLE.  $\text{AeO}, + \text{C}_4 \text{H}_3 \text{O}_3$ . This ether was discovered as far back as 1759 by the Count de Lauraguais. (*Mém. Acad. Par.*) It may be prepared, 1. by distilling a mixture of 63 parts of concentrated acetic acid and 17 of sulphuric acid, with 100 of alcohol; the receiver should be carefully cooled; 125 parts may be distilled over. 2. Another process consists in distilling 3 parts of acetate of potassa, 3 of absolute alcohol, and 2 of sulphuric acid, to dryness. The product is then mixed with one-fifth part of sulphuric acid, and by careful re-distillation, acetic ether equal in volume to the alcohol may be obtained. The results of these operations, contain free acid and alcohol; the former may be abstracted by lime or chalk, and the latter by chloride of calcium. 3. Bucholz recommends the distillation of a mixture of 2 parts of alcohol, 3 of oil of vitriol, and 6 of dried acetate of lead. Liebig uses 32 parts of dried acetate of lead, 10 of oil of vitriol, and 9 of alcohol. The distillate consists in these cases of a mixture of acetic ether, ether, acetic acid, and alcohol; sulphurous acid is also generally present. It is purified by agitating it with water and adding carbonate of soda as long as any effervescence ensues. The ether which separates is then dehydrated by means of chloride of calcium, and distilled, and the ether, which first passes over, is put aside. When the boiling point rises to  $165^\circ$ , pure acetic ether is obtained. In these processes an equivalent quantity of dry acetate of soda or acetate of potassa may be substituted for the acetate of lead.

Acetic ether boils, according to Dumas and Boullay, at about  $165^\circ$ . Its sp. gr. is 0.89, and the density of its vapor is 3.03. It has a peculiarly agreeable odor, and appears to exist in and contribute to the odor and flavor of certain wines. It burns with a yellowish flame, and acetic acid is developed by its combustion. Water dissolves about one-seventh of its weight of this ether, and the solution is decomposed by potassa, giving rise to an acetate, and to alcohol. Ammonia has no action upon it. It is soluble in all proportions in alcohol and in ether. Acetic ether is rapidly absorbed by a mixture of quicklime and caustic potassa, and



on the application of heat, hydrogen is evolved, and acetate of potassa remains. (DUMAS and STASS, *Ann. der Pharm.*, xxxv. 162.) It has been analysed by Dumas and Boullay (*Poggend. Ann.*, xii. 440, and *Ann. Ch. et Ph.*, xxxvii. 15), and by Liebig (*Poggend.*, xxvii. 616), with the following results:—

|                    |   |     |    |     |        |     |         | Dumas and<br>Boullay. |
|--------------------|---|-----|----|-----|--------|-----|---------|-----------------------|
| Carbon .....       | 8 | ... | 48 | ... | 54.55  | ... | 54.820  | 54.47                 |
| Hydrogen .....     | 8 | ... | 8  | ... | 9.09   | ... | 8.755   | 9.67                  |
| Oxygen .....       | 4 | ... | 32 | ... | 36.36  | ... | 36.425  | 35.86                 |
| <hr/>              |   |     |    |     |        |     |         |                       |
| Acetic ether ..... | 1 |     | 88 |     | 100.00 |     | 100.000 | 100.00                |

These elements are equivalent to

|              |   |     |    |     |       |               |             |     |     |     |     |    |
|--------------|---|-----|----|-----|-------|---------------|-------------|-----|-----|-----|-----|----|
| Etherine ... | 1 | ... | 28 | ... | 31.8  | } Ether ..... | 1           | ... | 37  | ... | 42  |    |
| Water .....  | 1 | ... | 9  | ... | 10.2  |               |             |     |     |     |     |    |
| Acetic acid  | 1 | ... | 51 | ... | 58.0  |               | Acetic acid | 1   | ... | 51  | ... | 58 |
| <hr/>        |   |     |    |     |       |               | <hr/>       |     |     |     |     |    |
| Acetic ether | 1 |     | 88 |     | 100.0 |               | 1           |     | 88  |     | 100 |    |

According to Pelouze, when carbonic acid is passed through an alcoholic solution of acetate of potassa, acetic ether and bicarbonate of potassa are formed; this is a curious instance of etherification at common temperatures; the insolubility of the bicarbonate in alcohol is probably concerned in the action.

*Acetal. Basic acetic ether.*  $3\text{AeO} + \text{C}_4\text{H}_3\text{O}_3$ . When alcohol contained in a saucer is covered by an open jar, and some moistened spongy platinum placed in watch glasses just above its surface, acid vapor is formed, which is absorbed by, or falls into, the alcohol, and gradually renders it very sour; if it be then distilled off powdered chalk, and subsequently rectified over chloride of calcium, *acetal* is obtained. (DÖBEREINER, *Poggend. Ann.*, xxiv. 603.) It is a colorless fluid, the odor of which resembles that of nitrous ether. Its specific gravity is 0.823. It boils at  $167^\circ$ . It dissolves in alcohol and ether, and in about 6 parts of water. It burns with a bright flame. By potassa, and by sulphuric acid, it is converted into a yellow resin. By the action of spongy platinum it forms acetic acid. According to Liebig's analysis (*Poggend. Ann.*, xxvii. 605) it consists of

|                |   |       |    |       |        |       | Liebig. |
|----------------|---|-------|----|-------|--------|-------|---------|
| Carbon.....    | 8 | ..... | 48 | ..... | 59.26  | ..... | 59.77   |
| Hydrogen ..... | 9 | ..... | 9  | ..... | 11.11  | ..... | 11.58   |
| Oxygen .....   | 3 | ..... | 24 | ..... | 29.63  | ..... | 28.65   |
| <hr/>          |   |       |    |       |        |       |         |
| Acetal .....   | 1 |       | 81 |       | 100.00 |       | 100.0   |

**BENZOIC ETHER. BENZOATE OF OXIDE OF ETHYLE.**  $\text{AeO} + \text{C}_{14}\text{H}_5\text{O}_3$ . This ether was discovered by Scheele; it may be obtained by subjecting a mixture of 4 parts of alcohol, 2 of benzoic acid, and 1 of hydrochloric acid, to distillation; when about half has passed over, it is returned into the retort, and the distillation is repeated in the same way two or three times. The *ether* is chiefly contained in the residue; it is washed with water, and then carefully distilled off finely powdered protoxide of lead. (THENARD, *Mém. d'Arcueil*, ii. 8.) Benzoic ether is an oily liquid, of a slight odor and pungent taste: its sp. gr. is 1.05; it

is insoluble in cold water, but soluble in alcohol and in ether. It boils at  $408^{\circ}$ , and yields a vapor, the sp. gr. of which is 5.2 (5.4, DUMAS and BOULLAY). It burns with a voluminous smoky flame.

A curious case of the production of this ether has been noticed by Wöhler and Liebig. (*Ann. Ch. et Ph.*, Li. 299.) When chloride of benzoic acid and alcohol are mixed, the temperature of the mixture rises so as to produce ebullition, hydrochloric acid is evolved, and on adding water to the residue, an oil-like substance separates, which is benzoic ether.

Benzoic ether consists of

|                  |      |    |      | Dumas<br>and<br>Boullay. |      | Wöhler<br>and<br>Liebig. |      |        |      |        |   |
|------------------|------|----|------|--------------------------|------|--------------------------|------|--------|------|--------|---|
| Carbon           | .... | 18 | .... | 108                      | .... | 72.0                     | .... | 72.40  | .... | 72.53  | } = { Ether 1 .... 37 .... 24.6<br>Benzoic }<br>acid } 1 .... 113 .... 75.4 |
| Hydrogen         | .... | 10 | .... | 10                       | .... | 6.7                      | .... | 6.57   | .... | 6.69   |   |
| Oxygen           | .... | 4  | .... | 32                       | .... | 21.3                     | .... | 21.03  | .... | 20.78  |   |
| <hr/>            |      |    |      |                          |      |                          |      |        |      |        |   |
| Benzoic<br>ether | }    | 1  |      | 150                      |      | 100.0                    |      | 100.00 |      | 100.00 |   |
|                  |      |    |      |                          |      |                          |      |        |      |        | 1 150 100.0   |

**HIPPURIC ETHER.** HIPPURATE OF OXIDE OF ETHYLE,  $\text{AeO} + \text{C}_{18}\text{H}_{18}\text{O}_5\text{N}$ , is formed by passing a current of hydrochloric acid gas through a solution of hippuric acid in alcohol, and heating the mixture for some time near to its boiling-point. The addition of water separates a thick, heavy oil, which when purified from alcohol and hydrochloric acid, and placed *in vacuo*, along with sulphuric acid, forms a solid crystalline mass, composed of silky needles. It is decomposed, like other *ethers*, by alkalis, and by boiling with water. (GREGORY.)

**SALICYLIC ETHER.** SALICYLATE OF OXIDE OF ETHYLE,  $\text{AeO} + \text{C}_{14}\text{H}_5\text{O}_5$ , is obtained by distilling 2 parts of alcohol,  $1\frac{1}{2}$  of salicylic acid, and 1 of sulphuric acid. When purified from alcohol, acid, and water, it is a colorless oily fluid, having a sweet smell like that of the corresponding compound of methyle, which occurs naturally in the oil of *Gaultheria procumbens*. It is heavier than water, and boils at  $437^{\circ}$ . Like the oil of *Gaultheria*, it plays the part of an acid, forming with bases crystallized soluble salts. When exposed to a high temperature with caustic baryta, it yields carbonic acid, and an oil analogous to that obtained from the methyle compound, probably  $\text{C}_{18}\text{H}_{10}\text{O}_2$ . When fuming nitric acid is added drop by drop to the salicylic ether, it dissolves it with a deep red color: water now separates an oil, which soon concretes into a solid mass, which when dissolved in hot alcohol, yields on cooling, yellow silky needles. These are *indigotate*, or *anilate of oxide of ethyle*,  $\text{C}_4\text{H}_5\text{O} + \text{C}_{14}\text{NH}_4\text{O}_9$ . By the further action of nitric acid, carbazotic or nitropicric acid is obtained. The indigotic ether dissolves in potash and soda, apparently like the salicylic ether, playing the part of an acid. Indigotic ether does not dissolve in ammonia: left in contact with it in close vessels, it finally disappears: alcohol is reproduced, and there is formed a new product, *anilamide*,  $\text{C}_{14}\text{N}_2\text{H}_6\text{O}_8$ , which, when pure, forms brilliant yellow crystals. When boiled with potash, anilamide yields anilate (indigotate) of potash, and gives off ammonia; for  $\text{C}_{14}\text{N}_2\text{H}_6\text{O}_8 + 2\text{HO} = \text{NH}_3 + \text{C}_{14}\text{H}_4\text{NO}_9, \text{HO}$ . Bromine acts on salicylic ether, pro-



ducing two compounds: monobromuretted salicylic ether,  $C_{18}H_9BrO_6 = C_4\left\{\begin{smallmatrix} H^4 \\ Br \end{smallmatrix}\right. O + C_{14}H_5O_5$ : and bibromuretted salicylic ether,  $C_{18}H_8Br_2O_6 = C_4\left\{\begin{smallmatrix} H^3 \\ Br_2 \end{smallmatrix}\right. O + C_{14}H_5O_5$ . The former crystallizes in fine needles: the latter in large pearly scales, which, when melted, form on cooling a most beautiful crystallization, formed of large and perfect cubes, like those of bismuth. (GREGORY. *Outlines of Chem.*, 363.)

SUCCINIC ETHER. SUCCINATE OF OXIDE OF ETHYLE.  $AcO, + C_4H_2O_3$ .

1. Dumas, upon the authority of F. D'Arcet, gives the following process for preparing this ether. Distil together 10 parts of succinic acid, 20 of alcohol, and 5 of concentrated hydrochloric acid, cohobating the distilled product four or five times; the residue in the retort will then consist of alcohol, water, succinic and hydrochloric acid, and succinic ether; when mixed with water, the succinic ether separates like heavy oily drops; it is collected, washed with cold water, boiled in a flask with a short neck till its boiling-point becomes constant, and lastly, distilled off dry protoxide of lead. 2. Fehling obtains succinic ether by passing hydrochloric acid gas into a boiling solution of succinic acid in absolute alcohol. On adding water to the resulting liquor, the impure ether separates, and may be washed, and then dehydrated by chloride of calcium, and distilled. (*Ann. der Pharm.*, xxxviii. 285, and xlix. 154.)

Succinic ether is a limpid, colorless, oily liquid, of an aromatic odor; and pungent flavor. Its specific gravity is 1.036. It boils at  $417^\circ$ ; the density of its vapor is 5.9. It is resolved by potassa into succinic acid and alcohol. Chlorine decomposes it under the influence of light, and forms crystals which have been examined by A. Cahours (*Ann. Ch. et Ph.*, 3ème Sér., Oct. 1843), according to whom they consist of  $C_{16}H_8O_8Cl_{13}$ . The ether consists of

|                |   |     |    |     | Fehling. |     |        |       |               |       |     |       |     |        |
|----------------|---|-----|----|-----|----------|-----|--------|-------|---------------|-------|-----|-------|-----|--------|
| Carbon.....    | 8 | ... | 48 | ... | 55.2     | ... | 55.72  | } = { | Ether .....   | 1     | ... | 37    | ... | 42.53  |
| Hydrogen ....  | 7 | ... | 7  | ... | 8.0      | ... | 8.16   |       | Succinic acid | 1     | ... | 50    | ... | 57.47  |
| Oxygen .....   | 4 | ... | 32 | ... | 36.8     | ... | 36.12  |       |               |       |     |       |     |        |
| <hr/>          |   |     |    |     | <hr/>    |     |        |       |               | <hr/> |     | <hr/> |     | <hr/>  |
| Succinic ether | 1 |     | 87 |     | 100.0    |     | 100.00 |       |               | 1     |     | 87    |     | 100.00 |

TARTARIC ETHER. TARTRATE OF OXIDE OF ETHYLE, may be obtained from 5 parts of tartaric acid, 7 of alcohol, 2 of sulphuric acid; distil the mixture till a little sulphuric ether begins to be formed. If at this period we withdraw the heat, the liquor assumes a syrupy consistence; but water does not separate the compound of the vegetable acid and alcohol. By adding, by degrees, solution of potassa, we throw down bitartrate of potassa; then, after having just saturated the redundant acid, if we evaporate the liquid, and treat it in the cold with very pure alcohol, we obtain, by evaporation of the alcoholic solution, a substance which, on cooling, becomes like syrup. This substance has a brown color, and a bitter and nauseous taste. It is void of smell and acidity, and is soluble in water and alcohol. It does not precipitate solution of chloride of calcium, but copiously that of chloride of barium. When heated, it diffuses dense fumes which have the odor of garlic, and at

the same time it leaves a residue, not alkaline, containing much sulphate of potassa. If distilled with potassa, it is resolved into a very strong alcohol, and much tartrate of potassa; it is, therefore, an ethereal combination. (THENARD, *Mém. d'Arcueil*, ii. 13.)

**TARTROVINIC ACID.**  $\text{AeO}, \text{HO}, + \text{C}_8 \text{H}_4 \text{O}_{10}$ . When pulverized tartaric acid is digested for six hours with its weight of anhydrous alcohol at a temperature between  $150^\circ$  and  $160^\circ$ , and then diluted with 4 parts of water, gently heated, and saturated by carbonate of baryta, tartrate of baryta falls, and the solution, evaporated at about  $110^\circ$  and filtrated, yields, on spontaneous evaporation, crystals of *tartrovinate of baryta*. This salt, when decomposed by an equivalent of dilute sulphuric acid, filtered, and evaporated *in vacuo*, leaves a white inodorous residue, which is *tartrovinic acid*: it has a sweetish acid taste, crystallizes in long oblique prisms, deliquescent, soluble in water and in alcohol, insoluble in ether, and burning with a pale flame; boiled for some hours with 40 parts of water, it is resolved into tartaric acid and alcohol. Subjected to a temperature of between  $300^\circ$  and  $400^\circ$ , it fuses and is decomposed, yielding alcohol, water, acetic ether, acetic acid, carbonic acid, carburetted hydrogen, a volatile oil, and a liquid resembling acetone; and a mixture of charcoal, pyrotartaric acid, and oily matter, remains in the retort.

Tartrovinic acid is decomposed when heated with nitric or sulphuric acid; it dissolves iron and zinc with the evolution of hydrogen; it has no action on tin.

The aqueous solution of tartrovinic acid dropped into baryta water, forms a precipitate, which gradually diminishes as the liquid approaches neutralization, and again increases on adding excess of the acid; this is not the case with tartaric acid; nitric acid redissolves the precipitates. Tartrovinic acid does not precipitate any solution of strontia; added to lime water, it throws down a precipitate soluble in excess of acid; it forms no precipitate under any circumstances, either with potassa or soda. With neutral acetate of lead it forms small nacreous prismatic crystals, insoluble in tartrovinic acid, but soluble in nitric acid. With a saturated solution of nitrate of silver it gives an insoluble precipitate. These characters distinguish the tartrovinic from the tartaric acid. (GUERIN-VARRY, *Ann. Ch. et Ph.*, LXii. 55.) Its ultimate components in its *anhydrous* state, as in the salts of silver, and baryta, are

|                                |    |     |     |     |       | Guerin-Varry. |
|--------------------------------|----|-----|-----|-----|-------|---------------|
| Carbon .....                   | 12 | ... | 72  | ... | 42.6  | 43.07         |
| Hydrogen .....                 | 9  | ... | 9   | ... | 5.3   | 5.27          |
| Oxygen .....                   | 11 | ... | 88  | ... | 52.1  | 55.66         |
| <hr/>                          |    |     |     |     |       |               |
| Anhydrous tartrovinic acid.... | 1  |     | 169 |     | 100.0 | 100.00        |

The *crystallized acid* consists of

|                                     |   |       |     |       |     |
|-------------------------------------|---|-------|-----|-------|-----|
| Anhydrous tartrovinic acid.....     | 1 | ..... | 169 | ..... | 95  |
| Water .....                         | 1 | ..... | 9   | ..... | 5   |
| <hr/>                               |   |       |     |       |     |
| Crystallized tartrovinic acid ..... | 1 |       | 178 |       | 100 |

The components of the anhydrous acid are therefore equivalent to 1 atom of tartaric acid (132) and 1 atom of ether (37); and those of



the crystallized acid are equivalent to 1 atom of tartaric acid, 1 of ether, and 1 of water; the former, therefore, is an *anhydrous* and the latter a *hydrated tartrate of ether*.

*Salts of the Tartrovinic Acid.* The *Tartrovinates* are soluble in water, and in hydrated alcohol, and sparingly soluble in anhydrous alcohol; they are mostly crystallizable, greasy to the touch, and burn with a flame resembling that of alcohol. They fuse when heated to between  $380^{\circ}$  and  $420^{\circ}$ , and are decomposed at a temperature a little above that of their point of fusion; the products of their decomposition are water, alcohol, acetic ether, acetic acid, a volatile oil, carburetted hydrogen, and carbonic acid, and charcoal remains in the retort, mixed, if the temperature has not been too high, with a pyrotartrate. Boiled in water the tartrovinates are resolved into water, alcohol, and acid tartrates. Heated with an alkali to between  $320^{\circ}$  and  $340^{\circ}$  they evolve alcohol, acetic ether, and a bitter oil. With the exception of the tartrovinatate of silver, they all contain water of crystallization, which may be abstracted by a dry vacuum. In the neutral tartrovinates, the oxygen in the acid is to that in the base as 11 to 1. When anhydrous, they may be regarded as compounds of 1 atom of anhydrous tartaric acid, 1 of ether, and 1 of base. They are obtained either by double decomposition, or by the mutual action of tartaric acid, alcohol, and a carbonate.

*Tartrovinatate of Potassa* is obtained by the decomposition of tartrovinatate of baryta, by slight excess of sulphate of potassa; evaporate the filtrated solution nearly to the consistence of syrup, and throw down undecomposed sulphate of potassa by alcohol, filter again, and evaporate spontaneously. It is a white, inodorous, bitterish salt, and crystallizes in truncated rhomboidal prisms; it is soluble in about its own weight of water at  $60^{\circ}$ , and in all proportions at  $212^{\circ}$ . This salt consists of

|   |   |     |     |     |       | Guérin-Varry. |
|---|---|-----|-----|-----|-------|---------------|
| Potassa .....                               | 1 | ... | 48  | ... | 21.2  | 20.83         |
| Tartrovinic acid .....                      | 1 | ... | 169 | ... | 74.8  | 75.17         |
| Water .....                                 | 1 | ... | 9   | ... | 4.0   | 4.00          |
| <hr/>                                       |   |     |     |     |       | <hr/>         |
| Crystallized tartrovinatate of potassa .... | 1 |     | 226 |     | 100.0 | 100.00        |

There is also a *basic tartrovinatate of potassa*, alkaline to reagents, and which crystallizes in octagonal prisms with polyhedral terminations, apparently resulting from an oblique base.

*Tartrovinatate of Soda* is prepared as the salt of potassa; it forms rhomboidal and rectangular lamellar crystals, which include 2 atoms of water.

*Tartrovinatate of Lime* is prepared as the salt of baryta; it forms white rectangular and lamelliform prisms, including 5 atoms of water of crystallization.

*Tartrovinatate of Baryta.* The preparation of this salt is described above; its primary form is an oblique rhomboidal prism; it is white, inodorous, and slightly bitter; its crystals include 2 atoms of water; 100 parts of water, at  $60^{\circ}$ , dissolve about 36 of this salt, and at  $212^{\circ}$ , 128 parts. It is insoluble in anhydrous alcohol.

*Tartrovinatate of Zinc* is produced by the action of the dilute acid on zinc; it is white, and crystallizes in rectangular prisms, greasy to the touch.

*Tartrovinatate of Copper* is formed by digesting oxide of copper in warm tartrovinic acid; it forms groups of silky prisms, including 6 atoms of water.

*Tartrovinat* of Silver is thrown down in the form of minute prismatic crystals, on mixing concentrated solutions of nitrate of silver, and of tartrovinat of potassa or baryta, the latter being in excess. The precipitate must be dried in the dark at a temperature not exceeding  $120^{\circ}$ , after having been washed with cold water, in which it is very sparingly soluble; it becomes red, and afterwards brown, when exposed to light. It consists of

|                            |   |      |     |      |       | Guerin-Varry. |        |
|----------------------------|---|------|-----|------|-------|---------------|--------|
| Oxide of silver .....      | 1 | .... | 116 | .... | 40.7  | ....          | 40.44  |
| Tartrovinic acid .....     | 1 | .... | 169 | .... | 59.3  | ....          | 59.56  |
| <hr/>                      |   |      |     |      |       | <hr/>         |        |
| Tartrovinat of silver .... | 1 |      | 285 |      | 100.0 |               | 100.00 |

RACEMOVINIC ACID. PARATARTROVINIC ACID.  $\text{AeO}, \text{HO}, + 2[\text{C}_4 \text{H}_2 \text{O}_5]$  The action of the racemic acid on alcohol corresponds with that of the tartaric, and the resulting *racemovinic acid*, as well as the salts which it forms, bear a general analogy to the corresponding tartrovinates. The composition of the *crystallized racemovinic acid* is  $= \text{AeO}, \text{HO}, + 2[\text{C}_4 \text{H}_2 \text{O}_5] + \text{HO}$ . (GUERIN-VARRY, *Ann. Ch. et Ph.*, lxii. 73.)

CITRIC ETHER. CITRATE OF OXIDE OF ETHYLE.  $3\text{AeO}, + \text{C}_{12} \text{H}_5 \text{O}_{11}$ . 1. When hydrochloric gas is passed into a hot saturated alcoholic solution of citric acid, and the resulting compound heated so as to expel chloride of ethyle and excess of hydrochloric acid, an impure citric ether remains, which may be purified by repeated washing, first with dilute solution of carbonate of soda, and then with water. (HELDT.) 2. When 1 part of citric acid, and 8 of absolute alcohol, are distilled till the temperature rises to  $358^{\circ}$ , and the distillate then returned into the retort, and the operation repeated till the boiling-point rises to  $374^{\circ}$ , the residue in the retort yields citric ether on mixture with water, which may be purified by agitation with weak solution of ammonia. (MITSCHERLICH.) 3. Distil a mixture of 100 parts of alcohol (sp. gr. 0.814), 50 of citric acid, and 50 of sulphuric acid, till streaks of ether appear; then dilute the residue in the retort with twice its volume of water, which precipitates the citric ether; wash it, dissolve it in alcohol, and decolor it by animal charcoal; lastly, expel the alcohol by evaporation, and dry the remaining citric ether *in vacuo*. (MALAGUTI.)

Citric ether is a colorless oily liquid, of an unpleasant bitter taste, and nearly inodorous. Its sp. gr. is 1.142. At  $266^{\circ}$  it becomes turbid; at  $518^{\circ}$ , reddish; and at  $540^{\circ}$  it is decomposed. It is sparingly soluble in water, but soluble in all proportions in alcohol. Alkalis resolve it into alcohol and citric acid. (LÖWIG, *Chem. der Organ. Verbind.*, ii. 1309.) Its formula, according to Dumas, is  $3\text{AeO} + \text{C}_{12} \text{H}_5 \text{O}_{11} = \text{C}_{24} \text{H}_{20} \text{O}_{14}$ ; but the analyses of Heldt and Malaguti assign to it an additional atom of water, representing it as  $3\text{AeO} + \text{C}_{12} + \text{HO}$ , its ultimate elements being

|                    |    |      |     |      |        | Heldt. | Malaguti. |
|--------------------|----|------|-----|------|--------|--------|-----------|
| Carbon .....       | 24 | .... | 144 | .... | 50.81  | ....   | 50.95     |
| Hydrogen .....     | 21 | .... | 21  | .... | 7.31   | ....   | 7.29      |
| Oxygen .....       | 15 | .... | 120 | .... | 41.88  | ....   | 41.76     |
| <hr/>              |    |      |     |      |        | <hr/>  |           |
| Citric ether ..... | 1  |      | 285 |      | 100.00 |        | 100.00    |



CENANTHIC ETHER.  $\text{AeO}, + [\text{C}_{14}\text{H}_{13}\text{O}_2]$  The presence of a peculiar compound upon which the fragrantcy and persistent odor of certain wines depends, has already been adverted to. Liebig and Pelouze have shown that this odorous principle is a compound of ether; that it is an *cenanthate of oxide of ethyle*. (*Ann. der Pharm.*, xix. 246.) Mulder has detected the same compound in the oil of grain-spirit, and in some other fermented liquors (*Ibid.*, xlv. 70, and *Poggend. Ann.*, xli. 582); and Wöhler supposes that quinces derive their distinctive perfume from it. (See also, in reference to these compounds, the results of the researches of Laurent, Bromeis, Tilley, &c., on *Cenanthylic acid*, derived from the action of nitric acid upon certain fat acids, at p. 1259.)

Cenanthic ether is obtained by agitating the oil derived from brandy or from grain-spirit (Weinfuselöl), which is a mixture of cenanthic acid and cenanthic ether, with a solution of carbonate of soda, till the free acid is neutralized; heat is then applied, and the cenanthic ether separates upon the surface, and may be dehydrated by chloride of calcium. It is an oily liquid, of a strong, and even intoxicating vinous odor, soluble in ether and in alcohol, but not in water: it is not decomposed by carbonate of potassa. The action of chlorine upon it has been studied by Malaguti. (*Ann. Ch. et Ph.*, lxx. 337, and *Erdmann and Marchand's Journ.*, xviii. 47.) The sp. gr. of cenanthic ether is 0.862, and the density of its vapor = 10.5. Its components are

|                      |         |     |           |     |           |     |              | Liebig and<br>Pelouze. |            |               |     |           |     |              |
|----------------------|---------|-----|-----------|-----|-----------|-----|--------------|------------------------|------------|---------------|-----|-----------|-----|--------------|
| Carbon .....         | 18      | ... | 108       | ... | 72        | ... | 72.02        | }                      | Ether..... | 1             | ... | 37        | ... | 24.66        |
| Hydrogen .....       | 18      | ... | 18        | ... | 12        | ... | 12.05        |                        |            |               |     |           |     |              |
| Oxygen .....         | 3       | ... | 24        | ... | 16        | ... | 15.93        |                        |            | Œnanthic acid | 1   | ...       | 113 | ...          |
| <hr/> Œnanthic ether | <hr/> 1 |     | <hr/> 150 |     | <hr/> 100 |     | <hr/> 100.00 |                        |            | <hr/> 1       |     | <hr/> 150 |     | <hr/> 100.00 |

#### COMBINATIONS OF ETHYLE WITH HALOGENS, OR OF ETHERINE WITH THE HYDRACIDS.

CHLORIDE OF ETHYLE. HYDROCHLORIC ETHER. MURIATIC ETHER.  $\text{C}_4\text{H}_5\text{Cl} = \text{Ae Cl}$ . *Sweet or dulcified spirit of salt*, was a favorite preparation with the old chemists; they conceived it to possess some peculiar solvent powers in regard to the salts of gold: it was also used in medicine: it was prepared in various ways; either by distilling a mixture of alcohol and hydrochloric acid; or of chloride of sodium, sulphuric acid, and alcohol. Its preparation by the action of alcohol upon chloride of tin was first described by the Marquis de Courtanvaux in 1768. (*Mém. de l'Acad. Royale des Sciences*, v. 19.)

*Chloride of ethyle* may be obtained by subjecting to careful distillation a concentrated solution of hydrochloric acid gas in alcohol; or a mixture of 1 part of alcohol, 1 of sulphuric acid, and 2 of fused and finely-powdered chloride of sodium; or a mixture of chloride of antimony, or of chloride of tin, and alcohol. In all these cases, chloride of ethyle passes over; it should first be transmitted into warm water, by which its adhering acid and alcohol are abstracted, and its vapor may then be condensed by conducting it through a cold tube, and receiving it in a bottle surrounded by ice and salt. Boullay's process for its preparation is as

follows. Absolute alcohol is saturated with dry hydrochloric gas, and the resulting liquor introduced into a flask connected with two Woulfes bottles, the first of which contains water at about  $80^{\circ}$ , while the second is immersed in a mixture of ice and salt. On applying heat to the flask, the vapors of alcohol and hydrochloric acid are retained in the first bottle, whilst the vapor of the ether goes over, and is condensed in the second.

Chloride of ethyle is a limpid, colorless liquid, of a peculiar penetrating odor, and a sweetish acrid flavor; it is neutral; its specific gravity is 0.874 at  $42^{\circ}$ : it boils at about  $60^{\circ}$ ; the specific gravity of its vapor is 2.219. When cooled down to  $-10^{\circ}$ , it crystallizes in cubes. It is soluble in about 50 parts of water, but soluble in all proportions in alcohol and in ether. It dissolves sulphur and phosphorus, and the fat and volatile oils. It forms a peculiar compound with anhydrous sulphuric acid, which has been examined by Kuhlmann. (*Ann. der Pharm.*, xxxiii. 108.) When exposed to the action of chlorine, under the influence of the sun's rays, it yields an extensive series of substitution compounds. With an alcoholic solution of protosulphuret of potassium, *sulphuret of ethyle* and chloride of potassium are formed.  $\text{Ac Cl} + \text{KS} = \text{AcS} + \text{KCl}$ . It burns with a flame tinged with green, and exhales the fumes of hydrochloric acid. Mixed with 4 volumes of oxygen and detonated by the electric spark, it yields 2 volumes of carbonic acid. It is very slowly altered by water and by alkalis. Passed through a red-hot tube, it is decomposed into hydrochloric acid, hydrocarbon, charcoal, and hydrogen. Its formula is  $\text{C}_4 \text{H}_5 \text{Cl}$ , or  $\text{C}_4 \text{H}_4 + \text{HCl}$ ; its components being

|                          |   |      |    |      |       | Dumas.     |
|--------------------------|---|------|----|------|-------|------------|
| Carbon.....              | 4 | .... | 24 | .... | 36.9  | .... 37.73 |
| Hydrogen .....           | 5 | .... | 5  | .... | 7.7   | .... 7.70  |
| Chlorine .....           | 1 | .... | 36 | .... | 55.4  | .... 54.57 |
| <hr/>                    |   |      |    |      |       |            |
| Chloride of ethyle ..... | 1 |      | 65 |      | 100.0 | 100.00     |

These elements are equivalent to

|                    |   |      |    |      |        |     |                    |   |      |    |      |       |
|--------------------|---|------|----|------|--------|-----|--------------------|---|------|----|------|-------|
| Ethyle.....        | 1 | .... | 29 | .... | 35.43  |     | Etherine.....      | 1 | .... | 28 | .... | 43.1  |
| Chlorine .....     | 1 | .... | 36 | .... | 54.57  | or, | Hydrochloric acid  | 1 | .... | 37 | .... | 56.9  |
| <hr/>              |   |      |    |      |        |     | <hr/>              |   |      |    |      |       |
| Chloride of ethyle | 1 |      | 65 |      | 100.00 |     | Chloride of ethyle | 1 |      | 65 |      | 100.0 |

*Chloral*. The mutual action of *chlorine and alcohol* was originally inquired into by Scheele and Westrumb; it afterwards engaged the attention of the principal chemists who have expounded the theory of etherification, and has been more recently investigated by Liebig and by Dumas. (*Ann. Ch. et Ph.*, xlix. 146; lvi. 113.) The resulting product was originally termed *heavy muriatic ether*; the term *chloral* (referring to chlorine and alcohol) has been applied to it by the last-mentioned chemists.

Chloral is obtained by passing a large quantity of chlorine, carefully dried, through anhydrous alcohol; the alcohol is at first kept cold, but when the first action is over, it requires to be gradually warmed; during the whole operation, which lasts several hours, hydrochloric acid



gas is evolved, and must be allowed to escape. Liebig found that several days were required to complete this action upon a quantity of alcohol amounting to about 8 ounces. The product of this operation is mixed with twice its bulk of sulphuric acid, and subjected to careful distillation; a limpid oil-like liquid passes over, which is to be heated in an open flask till its boiling-point attains about  $200^{\circ}$ ; it should then again be distilled off sulphuric acid, and finally rectified off a small quantity of fresh quicklime, the distillation being performed in a bath of salt and water.

Chloral is a transparent colorless liquid, of a greasy aspect; its specific gravity at  $65^{\circ}$  is 1.502; its boiling-point  $= 206^{\circ}$ ; and the density of its vapor about  $= 5.0$ . It has an irritating odor, is almost tasteless, somewhat caustic in its action upon the skin, soluble in water, neutral, and its solution is not affected by nitrate of silver. If, instead of dropping the chloral into water, and heating it to effect the solution, it be put into the contact of a few drops of water, the liquids combine into a white crystalline solid, and heat is evolved; and when a few drops of chloral are put into a flask containing humid air, small groups of crystals gradually form upon its interior; these are *hydrate of chloral*. When chloral is poured upon sulphuric acid, and left to itself, it forms a white substance, which Liebig calls *insoluble chloral*. Chloral dissolves iodine, bromine, sulphur, and phosphorus. When its vapor is passed over heated lime or baryta, those bases become incandescent, carbonic oxide is evolved, and metallic chlorides mixed with carbon remain. This sometimes happens in rectifying chloral over quicklime. The hydrated alkaline oxides decompose chloral. Nitric acid is almost without action upon it. Chloral consists of

|                |   |      |     |      |        | Dumas.    |
|----------------|---|------|-----|------|--------|-----------|
| Carbon .....   | 4 | .... | 24  | .... | 16.11  | .... 16.6 |
| Hydrogen ..... | 1 | .... | 1   | .... | 0.67   | .... 0.7  |
| Oxygen .....   | 2 | .... | 16  | .... | 10.74  | .... 10.8 |
| Chlorine ..... | 3 | .... | 108 | .... | 72.48  | .... 71.9 |
| <hr/>          |   |      |     |      |        |           |
| Chloral .....  | 1 |      | 149 |      | 100.00 | 100.0     |

*Hydrate of chloral* consists of 1 atom of chloral and 1 of water.

I must refer to Dumas (*Chim. app. aux Arts*, v. 608) for details of the theory of the various changes which alcohol undergoes during the action of chlorine, and the formation of chloral. The term *chloric ether* is sometimes applied to chloral, and to chloride of ethyle, and sometimes to the chloride of hydrocarbon described at page 543.

*Chloroform*.  $C_2HCl_3$ . Soubeiran and Liebig, by distilling chloral mixed with lime and water, or with solution of potassa, obtained a liquid, which when shaken with sulphuric acid, and then separated, and rectified over baryta, in a perfectly dry retort, yielded a dense limpid fluid, which has been designated *chloroform*. The same compound is obtained more easily by distilling a mixture of 1 pound of chloride of lime, 3 of water, and 3 ounces of alcohol, in a capacious retort; about 3 ounces of chloroform pass over. The term *chloroform* has reference to the constitution of *formic acid*, which is represented by  $C_2HO_3$ ; it is an oxide of a hydrocarbon  $= C_2H$ , to which the term *formyle* has been applied; so

that in reference to this view of its composition, chloroform is a *terchloride of formyle*. (See *Formyle*.)

The specific gravity of chloroform is 1.480 at 65°: it is very difficultly inflammable: its boiling-point about 140°: the density of its vapor = 4.2. When this vapor is respired it soon induces insensibility, in the same way as, but apparently more rapidly and effectually than ether vapor; hence its use in the performance of painful operations, as originally suggested by Dr. Simpson, of Edinburgh. (*Pharm. Journ.*, vii. 277 and 313.) When a few drops of chloroform are placed upon the hand, it speedily evaporates, and produces a great degree of cold. When poured upon water the greater part sinks in globules, which are of a milk-white appearance when the chloroform is not perfectly free from alcohol. It is so little soluble in water, that three drops added to nine ounces of distilled water, and well shaken, did not wholly disappear, although they imparted a strong odor to the liquid.

With *alcohol* and *ether* it readily forms transparent solutions, which burn with a yellow smoky flame. Water added to the alcoholic solution causes a separation of the chloroform, which falls to the bottom of the vessel.

Chloroform readily mixes and combines with *oil of turpentine*, and with *bisulphuret of carbon*. It easily dissolves *camphor*, and the solution burns with a yellow smoky flame, having a green edge or border. It speedily softens and dissolves *caoutchouc*, more readily when pure than when mixed with an equal part of oil of turpentine; although in the latter case the softening and solution are complete in twenty-four hours. It dissolves *amber*, *copal* (with great facility), and all the common *resins*. With red and black sealing-wax it makes a strong varnish. Contrary to the statement of Dumas, A. Taylor found that it did not perceptibly dissolve *sulphur* or *phosphorus*. It dissolves *wax*, and coagulates *albumen*.

Chloroform dissolves *iodine* and *bromine*, forming deep red solutions. A few drops of chloroform shaken with an aqueous solution of iodine or bromine will remove either of those bodies, and the chloroform falls to the bottom of the vessel, acquiring a red color, the depth of which is proportioned to the quantity of either substance present.

Chloroform floats on concentrated *sulphuric acid*, which is only darkened by it at a boiling temperature, when the chloroform is rapidly dissipated in vapor. It slowly decomposes *nitric acid* in the cold, but at a high temperature deoxidation is rapid, and nitrous acid is abundantly evolved. It scarcely affects a solution of *iodic acid*, which acquires, after a time, only a faint pink color. It has no bleaching properties: it does not decompose iodide of potassium, nor does it dissolve *gold*, either by itself or when boiled with concentrated nitric acid. When *nitrate of silver* is added to it, there is no precipitate, the chloroform merely acquiring that milky opacity which it has when dropped into distilled water.

It does not decompose chloride of gold on boiling.

When the vapor of chloroform is passed over copper or iron, heated to redness, it is decomposed, a metallic chloride results, and carbon is deposited; but, according to Liebig, no inflammable gas is evolved. It is not decomposed by potassium; some bubbles of hydrogen are sometimes



evolved, but it may be distilled over the metal without change. Caustic alkalis do not decompose it, except after long boiling, when it is entirely converted into chloride of potassium and formiate of potassa. Chloroform consists of

|                 |   |      |     |      |       |            |
|-----------------|---|------|-----|------|-------|------------|
|                 |   |      |     |      |       | Dumas.     |
| Carbon .....    | 2 | .... | 12  | ...  | 9.9   | .... 10.24 |
| Hydrogen .....  | 1 | .... | 1   | .... | 0.9   | .... 0.83  |
| Chlorine.....   | 3 | .... | 108 | .... | 89.2  | .... 88.93 |
| <hr/>           |   |      |     |      |       | <hr/>      |
| Chloroform .... | 1 |      | 121 |      | 100.0 | 100.00     |

IODIDE OF ETHYLE. HYDRIODIC ETHER.  $C_4 H_5 I = AeI$ . This compound was discovered by Gay-Lussac. (*Ann. Ch. et Ph.*, ix. 89.) It is best obtained by mixing in a retort, 4 parts of iodine, 10 of alcohol of 0.833, and gradually adding 2.5 of phosphorus: when the greater part has distilled over, 3 parts more of alcohol are put into the retort, and the distillation carried to dryness; the product is washed with cold water, and rectified over chloride of calcium.

*Iodide of ethyle* is colorless; it has a penetrating ethereal odor; its specific gravity at  $74^\circ$  is 1.92. It boils at  $148^\circ$ , and the density of its vapor is 5.409. It is not inflammable, but when dropped on red-hot charcoal it diffuses purple vapor. It is decomposed when passed through a red-hot tube, and among the products is an uctuous matter containing iodine. Exposed to air, it becomes red. It is sparingly soluble in water, but readily so in alcohol. Potassium does not decompose it; alkalis, nitric acid, and chlorine, only slowly act upon it; sulphuric acid rapidly decomposes it. It consists of

|                  |   |      |     |      |       |       |             |   |      |     |      |        |
|------------------|---|------|-----|------|-------|-------|-------------|---|------|-----|------|--------|
| Carbon .....     | 4 | .... | 24  | .... | 15.6  | } = { | Ethyle .... | 1 | .... | 29  | .... | 18.71  |
| Hydrogen .....   | 5 | .... | 5   | .... | 3.2   |       |             |   |      |     |      |        |
| Iodine.....      | 1 | .... | 126 | .... | 81.2  |       | Iodine .... | 1 | .... | 126 | .... | 81.20  |
| <hr/>            |   |      |     |      |       |       | <hr/>       |   |      |     |      |        |
| Iodide of ethyle | 1 |      | 155 |      | 100.0 |       |             | 1 |      | 155 |      | 100.00 |

or, of 1 atom of etherine + 1 hydriodic acid.

*Iodoform* is a compound analogous to *chloroform*, and obtained by a similar process; its formula is  $C_2 H, I_3$ . (SERULLAS and DUMAS, *Ann. Ch. et Ph.*, lvi. 133. See also *Formyle*.)

BROMIDE OF ETHYLE. HYDROBROMIC ETHER.  $C_4 H_5 Br = Ae Br$ .  
 1. To prepare this ether, introduce into a tubulated retort 40 parts of alcohol, specific gravity .827, and 1 of phosphorus, then add, gradually and carefully, 7 to 8 parts of bromine. The bromide of phosphorus which is formed, decomposes the water of the alcohol, and produces hydrobromic and phosphorous acids: distil by a gentle heat into a cooled receiver. When the distilled product is mixed with water, bromide of ethyle separates and falls to the bottom; if acid, it must be washed with a dilute solution of potassa. (SERULLAS, *Ann. Ch. et Ph.*, xxxiv. 95.)  
 2. Distil a mixture of 100 parts of bromide of potassium, 20 parts of absolute alcohol, and 36 parts of oil of vitriol: wash the product with water, and dehydrate it by chloride of calcium. (LÖWIG.)

*Bromide of ethyle* is colorless, transparent, of a strong ethereal odor, and a sweet and pungent taste. Its sp. gr. is 1.45. The density of its vapor = 3.975. It is very volatile, soluble in alcohol, and precipitated by water. When boiled with a solution of potassa *bromoform* is evolved, and formiate and bromide of potassium are produced.

The elements of bromide of ethyle are

|                       |   |     |     |     |        |       |              |   |     |     |     |     |
|-----------------------|---|-----|-----|-----|--------|-------|--------------|---|-----|-----|-----|-----|
| Carbon .....          | 4 | ... | 24  | ... | 22.43  | } = { | Ethyle ..... | 1 | ... | 29  | ... | 27  |
| Hydrogen .....        | 5 | ... | 5   | ... | 4.67   |       | Bromine..... | 1 | ... | 78  | ... | 73  |
| Bromine .....         | 1 | ... | 78  | ... | 72.90  |       |              |   |     |     |     |     |
| <hr/>                 |   |     |     |     |        |       |              |   |     |     |     |     |
| Bromide of ethyle.... | 1 |     | 107 |     | 100.00 |       |              | 1 |     | 107 |     | 100 |

*Bromoform*. Bromide of lime, distilled with water and alcohol, yields a product analogous to chloroform, which has been termed *bromoform* =  $C_2HBr_3$ . (DUMAS, *Ann. Ch. et Ph.*, Lvi. 113. See also *Formyle*.)

FLUORIDE OF ETHYLE. HYDROFLUORIC ETHER. Cold alcohol is saturated with hydrofluoric acid gas, and a fourth part is then distilled off: the distillate is mixed with twice its bulk of water, which separates the fluoride of ethyle. The operation must be performed either in platinum or leaden vessels. This ether is very volatile, colorless, burns with a blue flame evolving hydrofluoric acid, and has a peculiar odor resembling that of water-cresses. It cannot be kept in glass vessels. (REINSCH. *Erdmann and Marchand's Journ.*, xix. 314.)

CYANIDE OF ETHYLE. HYDROCYANIC ETHER.  $C_4H_5Cy$ . When equal parts of cyanide of potassium and sulphovinate of baryta are heated in a retort, a product is obtained, which, when washed with water, and agitated with, and then distilled off powdered chloride of calcium, yields *cyanide of ethyle*. (PELOUZE, *Jour. de Phar.*, xx.) In this operation, the water contained in the sulphovinate is decomposed, its oxygen is transferred to the potassium of the cyanide, and its hydrogen to the cyanogen to produce *hydrocyanic acid*, which, with the *hydrocarbon* of the sulphovinate, forms this ether.

Cyanide of ethyle is colorless, and has a strong alliaceous odor; its specific gravity is 0.70°; it boils at 180°. The density of its vapor is 1.912. When pure it does not affect a solution of nitrate of silver, and it is with difficulty decomposed by solution of potassa. It dissolves in all proportions in alcohol and in ether. It is sparingly soluble in water. It is poisonous, but less so than hydrocyanic acid. It consists of

|                   |       |     |       |     |       |       |             |       |     |       |     |       |
|-------------------|-------|-----|-------|-----|-------|-------|-------------|-------|-----|-------|-----|-------|
| Carbon.....       | 6     | ... | 36    | ... | 65.5  | } = { | Ethyle .... | 1     | ... | 29    | ... | 52.7  |
| Hydrogen .....    | 5     | ... | 5     | ... | 9.1   |       | Cyanogen    | 1     | ... | 26    | ... | 47.3  |
| Nitrogen .....    | 1     | ... | 14    | ... | 25.4  |       |             |       |     |       |     |       |
| <hr/>             | <hr/> |     | <hr/> |     | <hr/> |       | <hr/>       | <hr/> |     | <hr/> |     | <hr/> |
| Cyanide of ethyle | 1     |     | 55    |     | 100.0 |       |             | 1     |     | 55    |     | 100.0 |

SULPHOCYANIDE OF ETHYLE. SULPHOCYANIC ETHER.  $Ae + CyS_2$ . By distilling a mixture of 1 part of sulphocyanide of potassium, 2 of sulphuric acid, and 3 of anhydrous alcohol, Liebig obtained a compound consisting apparently of sulphuret of cyanogen and etherine. (*Ann. Ch. et Ph.*, xli. 202.) Löwig gives the following directions for the prepara-



tion of *sulphocyanide of ethyle*. (*Chem. der Org. Verbind.*, ii. 1436.) A concentrated alcoholic solution of sulphocyanide of potassium is saturated with chloride of ethyle, and set aside for some weeks; the mutual decomposition goes on most rapidly in the sunshine: when it is complete, the liquor is mixed with its volume of water, and distilled. The distillate is mixed with twice its volume of ether, and water is then added, so as again to separate the ether, which now holds the sulphocyanide of ethyle in solution. This is then distilled, and the ether first passes over, and afterwards the sulphocyanide, which must be separately collected, and again distilled with water. It then passes over in oil-like drops floating about in the water, which collect upon the surface on the addition of chloride of calcium; the product is then collected, and, having been dehydrated by chloride of calcium, is distilled.

According to Cahours, this sulphocyanide is obtained by distilling a mixture of sulphovinate of lime and sulphocyanide of potassium in concentrated solution; it separates from the distillate, and requires to be deprived of water by chloride of calcium.

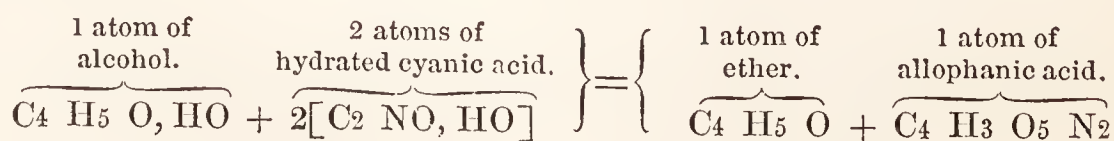
*Sulphocyanide of ethyle* is a colorless and highly refractive liquid, of a sweet anise-like taste, and a penetrating odor. Its specific gravity is 1.02. It boils at about 295°, and the density of its vapor is 3.018. (CAHOURS.) It combines energetically with nitric acid, forming a coupled sulpho-acid, which is colorless, and produces highly crystalline salts. It consists of

|                         |   |     |    |     |        |       |                |   |     |    |     |        |  |
|-------------------------|---|-----|----|-----|--------|-------|----------------|---|-----|----|-----|--------|--|
| Carbon .....            | 6 | ... | 36 | ... | 41.38  | } = { | Ethyle .....   | 1 | ... | 29 | ... | 33.33  |  |
| Hydrogen .....          | 5 | ... | 5  | ... | 5.74   |       | Sulphocyanogen | 1 | ... | 58 | ... | 66.67  |  |
| Nitrogen .....          | 1 | ... | 14 | ... | 16.11  |       |                |   |     |    |     |        |  |
| Sulphur .....           | 2 | ... | 32 | ... | 36.77  |       |                |   |     |    |     |        |  |
| <hr/>                   |   |     |    |     |        |       |                |   |     |    |     |        |  |
| Sulphocyanide of ethyle | 1 |     | 87 |     | 100.00 |       |                | 1 |     | 87 |     | 100.00 |  |

ALLOPHANIC ETHER. ALLOPHANATE OF OXIDE OF ETHYLE. When the vapor of hydrated cyanic acid is passed into alcohol, crystals are deposited which were represented by Liebig and Wöhler, (*Ann. der Pharm.*, lix. 291,) by the formula  $C_{24}H_{24}O_{18}N_6$ , and as containing the elements of

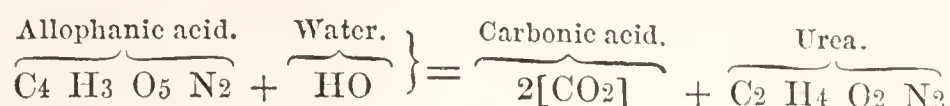
|                                |                         |
|--------------------------------|-------------------------|
| 3 atoms of alcohol.....        | $C_{12} H_{18} O_6$     |
| 2 „ hydrated cyanic acid ..... | $C_{12} H_6 O_{12} N_6$ |
| <hr/>                          |                         |
| $C_{24} H_{24} O_{18} N_6$     |                         |

They now consider this compound as consisting of oxide of ethyle combined with a new acid which they call *allophanic acid*, and to which they assign the formula  $C_4 H_3 O_5 N_2$ ; they consider it as formed by the union of 2 atoms of hydrated cyanic acid with 1 atom of water derived from the alcohol, while the oxide of ethyle thus produced combines with the new acid.



Allophanic acid forms crystallizable salts with potassa, soda, and baryta, and when we attempt to isolate the acid from these salts by a

stronger acid, it is immediately resolved, with the aid of an atom of water, into carbonic acid and urea.



The same transformation ensues when the solutions of the allophanates are heated. (*Turner's Elements of Chemistry*, 8th edit., 894.)

SULPHURET OF ETHYLE,  $\text{AeS}$ , is obtained by passing the vapor of chloride of ethyle through an alcoholic solution of protosulphuret of potassium; chloride of potassium is precipitated, and the liquid contains *sulphuret of ethyle*, which separates on the addition of water; its sp. gr. is 0.825; it has an alliaceous odor; it boils at  $153^\circ$ , and the sp. gr. of its vapor is 3.100.

HYDROSULPHURET OF SULPHURET OF ETHYLE. HYDROSULPHURIC ETHER. MERCAPTAN.  $\text{AeS} + \text{HS}$ . (ZEISE, *Ann. Ch. et Ph.*, xxxv. 87.) When sulphovinate of baryta is distilled with a concentrated solution of hydrosulphuret of sulphuret of barium, an ethereal liquid passes over, whilst the sulphovinate becomes a sulphate; this liquid floats upon the water; it is to be washed, and digested upon powdered chloride of calcium.  $[\text{BaO}, \text{AeO}, 2\text{SO}_3] + \text{BaS}, \text{HS} = \text{AeS}, \text{HS} + 2[\text{BaO}, \text{SO}_3]$

Liebig prepares this compound as follows: a solution of caustic potassa, sp. gr. 1.28 to 1.3, is saturated with sulphuretted hydrogen, and this solution of  $\text{KS}, \text{HS}$  is mixed with a concentrated solution of sulphovinate of potassa, and the mixture distilled in a water-bath; the product is *hydrosulphuret of sulphuret of ethyle*, and a little sulphuretted hydrogen. This distillate is then rectified over a little ethersulphuret of mercury (mercaptide of mercury) to abstract the sulphuretted hydrogen, and is dehydrated by digestion with chloride of calcium. The hydrosulphuretted salts of barium or calcium may be substituted for that of potassium. The original process of Zeise consists in the decomposition of mercaptide of mercury by sulphuretted hydrogen.  $\text{AeS HgS} + \text{HS} = \text{HgS} + \text{AeS}, \text{HS}$ .

The term *mercaptan* has been applied to this substance, in consequence of its energetic affinity for mercury (*mercurio aptum*), and however objectionable, it has brevity to recommend it: its compounds are termed *Mercaptides*.

*Mercaptan* is a colorless liquid, of a penetrating alliaceous odor and taste; it is very sparingly soluble in water, but dissolves in alcohol and in ether in all proportions. It does not congeal at  $8^\circ$ . Its sp. gr. is 0.832. It boils at about  $97^\circ$ , and the density of its vapor is  $= 2.14$ . It absorbs nitric oxide gas, and forms with it a red fuming liquor, which, exposed to light and air, gradually loses the whole of the nitric oxide. Acted upon by potassium or sodium, it gives off sulphuretted hydrogen, and sulphurets of ethyle and of the metals are formed. The alcoholic and aqueous solutions of mercaptan produce lemon-yellow precipitates in solution of acetate, but not of nitrate of lead. This precipitate is redissolved by excess of the precipitant, and the solution yields yellow acicular and lamellar crystals of a *mercaptide of lead*  $= \text{Pb} + \text{AeS}_2$ . The





# § XVI. PRODUCTS OF THE OXIDIZEMENT OF ALCOHOL. ACETYLE AND ITS COMPOUNDS.

When wine, beer, or similar liquors, in which vinous fermentation has ceased, are exposed to the access of air, and to a due temperature (above  $65^{\circ}$ ), a new fermentation ensues, in which oxygen is absorbed, and the alcohol gradually passes into *acetic acid*. This acid as it exists in combination with certain bases, has the formula  $C_4 H_3 O_3$ ; but in this, its *anhydrous* state, it has not been isolated; combined however with an atom of water, it constitutes an intensely sour *hydrate*, which, in consequence of its solidifying at a temperature of about  $45^{\circ}$ , is frequently termed *glacial acetic acid*, and is represented by  $C_4 H_4 O_4$ , or by the rational formula,  $C_4 H_3 O_3 + HO$ .

*Anhydrous acetic acid*, therefore, is composed of

|                           |   |     |    |     |        | Prout. | Berzelius. |
|---------------------------|---|-----|----|-----|--------|--------|------------|
| Carbon .....              | 4 | ... | 24 | ... | 47.06  | ...    | 47.05      |
| Hydrogen .....            | 3 | ... | 3  | ... | 5.88   | ...    | 5.88       |
| Oxygen .....              | 3 | ... | 24 | ... | 47.06  | ...    | 47.07      |
| <hr/>                     |   |     |    |     |        |        |            |
| Anhydrous acetic acid.... | 1 |     | 51 |     | 100.00 |        | 100.00     |
|                           |   |     |    |     |        |        | 46.83      |
|                           |   |     |    |     |        |        | 6.35       |
|                           |   |     |    |     |        |        | 46.82      |
| <hr/>                     |   |     |    |     |        |        |            |
|                           |   |     |    |     |        |        | 100.00     |

And the *glacial hydrate* consists of

|                           |   |     |    |     |        |       |                |       |     |     |     |     |
|---------------------------|---|-----|----|-----|--------|-------|----------------|-------|-----|-----|-----|-----|
| Carbon .....              | 4 | ... | 24 | ... | 40.00  | } = { | Anhydrous acid | 1     | ... | 51  | ... | 85  |
| Hydrogen .....            | 4 | ... | 4  | ... | 6.67   |       |                |       |     |     |     |     |
| Oxygen .....              | 4 | ... | 32 | ... | 53.33  |       | Water          | ..... | 1   | ... | 9   | ... |
| <hr/>                     |   |     |    |     |        |       |                |       |     |     |     |     |
| Hydrated acetic acid .... | 1 |     | 60 |     | 100.00 |       |                |       |     | 1   |     | 100 |
| <hr/>                     |   |     |    |     |        |       |                |       |     |     |     |     |

*Alcohol* consists of  $C_4 H_6 O_2$ ; so that its conversion into *anhydrous acetic acid* consists in the abstraction of 3 atoms of hydrogen, and the assumption of 1 atom of oxygen. But it is convenient, in reference to certain derivatives of acetic acid, to consider it as a compound of oxygen, with an acidifiable base  $= C_4 H_3$ . This base, which has not been isolated, has been termed *acetylene* ( $= Ac$ ), and may be derived from *ethyle*,  $C_4 H_5$ , by the abstraction of 2 atoms of hydrogen. In reference to this hypothesis, the members of the *acetylic series* will stand as follows:

|  |                    |
|--|--------------------|
| Acetylene .....                                | $C_4 H_3$          |
| Oxide of acetylene .....                       | $C_4 H_3 O$        |
| Hydrate of oxide of acetylene [aldehyde] ..... | $C_4 H_3 O + HO$   |
| Aldehydic acid [acetylous acid] .....          | $C_4 H_3 O_2 + HO$ |
| Acetic acid [acetylic acid] .....              | $C_4 H_3 O_3 + HO$ |

The two first members of this series, corresponding with ethyle and ether in the ethylic series, are unknown. The substance termed *aldehyde*, is the *alcohol of the acetylic series*, the further oxidizement of which produces the *aldehydic* and *acetic acids*.

ALDEHYDE. HYDRATE OF OXIDE OF ACETYLE.  $C_4 H_4 O_2$ ; or  $C_4 H_3 O + HO = AcO + HO$ . The term *aldehyde* is derived from *alcohol dehydrogenatus*, inasmuch as alcohol becomes aldehyde by the loss of 2 atoms of hydrogen. Aldehyde has already been adverted to, as forming, under certain conditions, one of the products of the decomposi-



tion of ether and of alcohol, as in the case of passing ether vapor through a red-hot tube, or burning mixtures of ether or alcohol-vapor and oxygen, at comparatively low temperature and without flame. (p. 129.) It is best obtained in its pure state by the following process. (LIEBIG. *Ann. Ch. et Ph.*, Lix. 289.) A mixture of 4 parts of alcohol (sp. gr. 0·844), 6 of oil of vitriol, 4 of water, and 6 of pulverised binoxide of manganese, is introduced into a capacious retort, and distilled through a condenser into a large receiver cooled by ice; when about 6 parts have passed over, or when the distillate becomes sour, the process is stopped, and the product is put into a small retort with about its own weight of chloride of calcium, and redistilled; and this process is repeated, so as to yield about 3 parts of dehydrated aldehyde; it however still contains acetal, ether, and alcohol; to free it from these, it is mixed with about twice its volume of ether, and saturated with dry gaseous ammonia, when a crystalline compound of aldehyde and ammonia gradually separates, which is insoluble in ether, and which may be dried in the air. Two parts of this compound are then dissolved in their weight of water, and the solution mixed with 3 parts of sulphuric acid previously diluted by 4 of water, and distilled. Considerable effervescence ensues during the evolution of the aldehyde, which requires to be passed through a good condensing apparatus; the distillate is finally dehydrated by the careful addition of a little chloride of calcium, and distilled at a temperature of about 87°.

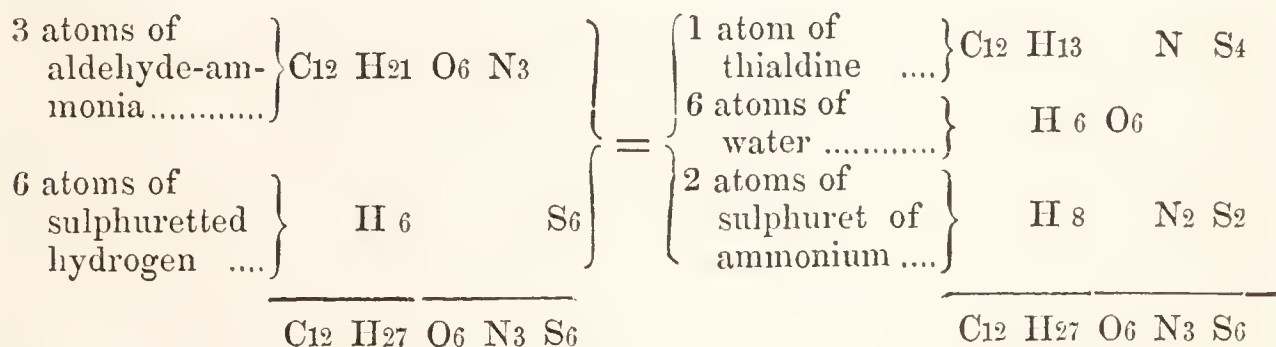
Pure aldehyde is a very mobile and volatile colorless liquid, of a peculiar ethereal, and at the same time suffocating odor; when its vapor is respired it produces spasm of the organs of breathing. Its sp. gr. is 0·79 at 65°. It mixes in all proportions with water, alcohol, and ether, and may be separated from its aqueous solution by means of chloride of calcium. It is neutral to test paper, but acquires acidity on exposure to air, in consequence of the formation of acetic acid, a change which is very rapid under the influence of platinum-black. Heated with dilute nitric acid it is also acetified, and nitrous acid is formed. An aqueous solution of aldehyde heated with oxide of silver reduces the metal in the form of a brilliant film, and *aldehydate of silver* is found in solution.  $2\text{AgO} + \text{AcO}, \text{HO} = \text{AgO}, \text{AcO}_2, \text{HO} + \text{Ag}$ . When the solution of aldehydate of silver is mixed with baryta water, oxide of silver is precipitated, and *aldehydate of baryta* retained in solution. If the liquor containing the precipitated oxide of silver be warmed, metallic silver is thrown down, and acetate of baryta is found in the solution.  $\text{BaO}, \text{AcO}_2, + \text{AgO}, = \text{BaO}, \text{AcO}_3, + \text{Ag}$ . When aldehyde vapor is passed over a heated mixture of hydrate of potassa and quicklime, acetate of potassa is formed, and hydrogen gas disengaged.  $\text{AcO}, \text{HO}, + \text{HO} = \text{AcO}_3 + \text{H}_2$ . (DUMAS and STASS. *Ann. der Pharm.*, xxxv. 161.) When aldehyde is heated with a solution of caustic potassa, a brown resinous substance is formed, called by Liebig, *Aldehyde-resin*. The components of aldehyde are

|                |   |       |    |       |        |              |
|----------------|---|-------|----|-------|--------|--------------|
|                |   |       |    |       |        | Liebig.      |
| Carbon .....   | 4 | ..... | 24 | ..... | 54·54  | ..... 54·642 |
| Hydrogen ..... | 4 | ..... | 4  | ..... | 9·09   | ..... 9·008  |
| Oxygen .....   | 2 | ..... | 16 | ..... | 36·37  | ..... 36·350 |
| <hr/>          |   |       |    |       |        | <hr/>        |
| Aldehyde.....  | 1 |       | 44 |       | 100·00 | 100·000      |

ALDEHYDE-AMMONIA.  $\text{NH}_4\text{O}, + \text{AcO} = \text{NII}_3, \text{AcO}, \text{IIO}$ . The preparation of this compound has been above described. It crystallises in acute rhomboids, which are colorless, transparent, highly refractive, and brittle; they have a peculiar flavor resembling a mixture of ammonia with turpentine; they are inflammable, fusible between  $160^\circ$  and  $175^\circ$ , and volatile at  $212^\circ$  without decomposition. They gradually acquire a yellow tint, especially when exposed to light. Water dissolves this compound in all proportions, but it is sparingly soluble in alcohol, and insoluble in ether. When a concentrated solution of aldehyde-ammonia is mixed with one of nitrate of silver, a white precipitate falls, soluble in water, and sparingly soluble in alcohol, composed of 4 atoms of aldehyde, 2 of ammonia, 1 of nitric acid, and 2 of oxide of silver. When the solution is heated, aldehyde and ammonia are evolved, and part of the silver is thrown down in the metallic form. Oxide of silver heated with aldehyde-ammonia is reduced. The components of aldehyde-ammonia are

|                  |       |        |           |         |       |               |                |        |        |
|------------------|-------|--------|-----------|---------|-------|---------------|----------------|--------|--------|
|                  |       |        |           | Liebig. |       |               |                |        |        |
| Carbon .....     | 4 ... | 24 ... | 39·34 ... | 39·817  | } = { | Ammonia 1 ... | 17 ...         | 27·87  |        |
| Hydrogen .....   | 7 ... | 7 ...  | 11·49 ... | 11·472  |       |               |                |        |        |
| Oxygen .....     | 2 ... | 16 ... | 26·23 ... | 25·992  |       |               |                |        |        |
| Nitrogen .....   | 1 ... | 14 ... | 22·94 ... | 22·719  |       |               | Aldehyde 1 ... | 44 ... | 72·13  |
| <hr/>            |       |        |           |         |       |               |                |        |        |
| Aldehyde-Ammonia | 1     | 61     | 100·00    | 100·000 |       |               | 1              | 61     | 100·00 |

When an aqueous solution of aldehyde-ammonia, to which a little excess of ammonia has been added, is subjected to the action of sulphuretted hydrogen, crystals are deposited which have basic properties. This substance, called *Thialdine*,  $=\text{C}_{12}\text{H}_{13}\text{NS}_4$ , is the result of the mutual action of 3 atoms of aldehyde-ammonia and 6 of sulphuretted hydrogen.



Thialdine is readily soluble in alcohol and in ether, but scarcely soluble in water. Its ethereal solution deposits it in large crystals, volatile, fusible, and of a peculiar odor. It neutralizes the acids and forms with them crystalline salts. Heated with hydrate of lime, it yields *leucoline*, one of the volatile bases of coal tar.

With seleniuretted hydrogen aldehyde-ammonia yields *Selenaldine*, and with telluretted hydrogen *Telluraldine*. (LIEBIG and WÖHLER.)

ALDEHYDIC ACID. ACETYLIOUS ACID.  $C_4 H_3 O_2$ , = Ac  $O_2$ . The arguments in favor of the existence of this acid are principally founded upon the phenomena attendant upon the action of oxide of silver upon



aldehyde, above adverted to; but there are several other cases in which it appears to be formed, and more especially during the slow combustion of ether which ensues when it is dropped upon a brick or other convenient surface heated up to between  $250^{\circ}$  and  $300^{\circ}$ , or when it is burned without flame under the influence of heated platinum (p. 129.) The acrid irritating vapor which is then formed, appears to be a mixture of acetic and aldehydic acid. This product was first examined by Daniell, who gave it the name of *lampic acid* (p. 1671), and afterwards regarded it as a mixture of formic and of acetic acid; but it possesses properties distinct from those acids, which are apparently referable to the presence of aldehydic acid.

When the vapor resulting from the above-mentioned slow combustion of ether is condensed, it constitutes a pungent acid liquid, which forms aldehyde-ammonia when its solution in ether is saturated by ammoniacal gas; but if it be saturated by oxide of lead, and the resulting lead-salts decomposed by sulphate of copper, sulphate of lead is formed, together with a soluble copper-salt, consisting partly of acetate of copper, and partly of a paler salt, of a disagreeable odor. When the solution of the latter is heated to  $212^{\circ}$ , suboxide of copper is thrown down, and acetate of copper formed. When the acid liquid is heated with binoxide of manganese, violent effervescence ensues, and abundance of carbonic acid gas is evolved.

When acetate of oxide ethyle (acetic ether) is acted upon by potassium, much heat is evolved, and a white flocculent salt is formed, which is probably *aldehydate of potassa*,  $= [\text{KO}, \text{AcO}_2]$ , for when it is distilled with acetic acid, a sour liquor passes over, which rapidly absorbs oxygen, and when cold dissolves oxide of silver; but, on the application of a little heat the solution deposits metallic silver, and acetic acid is formed in it.

ACETIC ACID. ACETYLIC ACID.  $\text{C}_4 \text{H}_4 \text{O}_4, = \text{C}_4 \text{H}_3 \text{O}_3 + \text{HO}$ ; or  $\text{AcO}_3, + \text{HO}$ ; (or  $\bar{\text{A}}$ ). It has been above stated that this acid is produced by the action of air upon wine, beer, and similar fermented liquors; but alcohol itself, or a mixture of alcohol and water, undergoes no change unless yeast, gluten, or some similar azotised organic matter be at the same time present: hence also the more perfect wines do not become sour, even when exposed to air, because, they contain no ferment.

Although in this mode of producing acetic acid, alcohol is its common source, there are other vegetable substances from which it may be obtained, independent of *vinous* fermentation; as from certain mucilaginous and amylaceous solutions containing vegetable albumine; and when once acetic acid is present, it hastens acetic fermentation, hence the necessity of great cleanliness in regard to the casks and vessels used in vinous fermentation, and in the preservation of wine and beer.

The action of yeast, and similar substances, in the conversion of alcohol into vinegar, that is, in causing it to absorb oxygen, is referred by Liebig to a process resembling that by which sulphurous, is converted into sulphuric acid, by the action of nitric oxide: the ferment, it is presumed, absorbs oxygen from the atmosphere and transfers it to the alcohol; but

the ferment itself gradually changes and becomes insoluble in water. "Some ascribe the acetification of alcohol to a new process called *catalysis*, by which mere *contact* is supposed to cause combinations and decompositions; but the same explanation would apply to the action of nitric oxide in the production of sulphuric acid, were it not that the visible formation and decomposition of nitrous acid betray the real nature of the change: there is, therefore, no occasion to assume a new and mysterious power, as it is evident that the organic matters alluded to induce acetification, as the powder of platinum does, by absorbing and condensing oxygen, so as to enable the alcohol to combine with it."

VINEGAR. This term is applied to the *dilute acetic acid*, which is chiefly employed for domestic consumption, and which varies extremely in strength, flavor, and composition, according to the sources whence it is obtained. In wine countries it is procured by exposing weak wines to the access of air at a due temperature, and its strength, flavor, and color, depend upon the characters of the wine employed. According to Dumas (*Chim. app. aux Arts*, vi. 536,) the best French vinegar is made of good wine, which is put into a cask already containing a portion of vinegar, and to which air has due access. As acetification goes on, more wine is added at intervals, and when the whole has become vinegar, it is drawn off to the amount of the wine employed, and the process is repeated. The temperature of the factory is maintained at about 86°. In this country *beer* is sometimes used as a source of vinegar; or a *wort* is prepared for the purpose; and, in these cases, the product acquires peculiarities dependant upon the foreign matters necessarily present. A good extemporaneous vinegar may be made by dissolving 1 part of sugar in 6 parts of water, and adding 1 of brandy or other strong spirituous liquor, and a little yeast: this mixture is put into a sufficiently large cask, with the bung-hole left open, and exposed to a temperature of between 70° or 80°; in a month or six weeks, the clear vinegar may be drawn off. Liebig recommends 100 parts of water, 13 of brandy, 4 of honey, and 1 of tartar; or 120 of water, 12 of brandy, 3 of brown sugar, 1 of tartar, and  $\frac{1}{2}$  of sour dough, left for some weeks in a warm place, as good ingredients for the production of vinegar.

The production of acetic acid by the slow combustion of alcohol has been above alluded to; Mitscherlich compares its formation by the exposure of alcohol, water, and a ferment, to air, to that process, as illustrated more especially in the improved method of acetification, in which vinegar may be made in three or four days, instead of requiring, as by the old method, more than as many weeks. This process, which was originally suggested by Glauber, (BOERHAAVE. *Elem. Chem.*, ii. 209. Leyden, 1732,) consists in suffering "a mixture of 1 part of alcohol and 8 or 9 of water, with a little yeast, to trickle through beech shavings previously soaked in vinegar, and lying loosely in a cask perforated full of holes; he says that the air loses so much oxygen, that if collected as it issues from the upper holes, it extinguishes flame, and that the temperature of the liquid rises to 85°, when that of the atmosphere is only 60°; that by the first operation, half the alcohol is acetified; and that the acetification is complete by a repetition of the process, provided



it be slowly conducted; and that vinegar may be made in this way in a few hours." (MITSCHERLICH.)

According to Liebig, the best proportions are, 1 part of alcohol (sp. gr. 0·848) with 4 to 6 of water, and a thousandth part of ferment, honey, or extract of malt; this mixture, previously heated to about  $80^{\circ}$ , is made to trickle through the shavings steeped in vinegar; it soon rises to  $100^{\circ}$  or  $104^{\circ}$ , and remains stationary at about that temperature, when all goes on favorably. When the liquid has been three or four times passed through the shavings, it is completely acetified, and this may be done in from 20 to 36 hours. All fermented liquors may be acetified in this way. When the supply of air is deficient, part of the alcohol remains in the state of aldehyde, which being volatile, escapes, and occasions a proportionate loss of acetic acid. The presence of essential oils, or the smallest trace of pyroligneous acid, prevents the acetification of the alcohol. (TURNER'S *Chemistry*, 8th edit., p. 912. See also a paper on the manufacture of vinegar, in the *Chemical Gazette* for January, 1843, pp. 153 and 188; *Neale's patent* for the manufacture of vinegar from beet-root: *ibid*, p. 167; and a memorandum on the subject, by F. Ham, *Chem. Gaz.*, i. 271. Several of the processes for the production of vinegar have also been described by Dr. Ure in a communication to the *Pharmaceutical Journal*, vii. pp. 285 and 328.)

In all these cases, the principle of acetification is the same, and consists in the formation of alcohol, and its subsequent conversion into acetic acid by the abstraction of hydrogen, as above explained. Air must always, therefore, have access; but the vessels should not be too open, because in that case acid is lost by evaporation, as the temperature is necessarily high.

Vinegar is apt to be infested by *flies* (*Musca cellaris*), and by animalcules, commonly termed *eels* (*Vibrio aceti*): these may be destroyed by passing it through a spiral tube immersed in water heated to  $212^{\circ}$ ; or by heating it in a hot-water bath. When vinegar is exposed to air, it gradually becomes turbid, or *mothery*, losing its acidity, and depositing a slippery gelatinous substance, which, when collected and dried, resembles gum, and is destitute of nitrogen; it does not, therefore, resemble animal mucus, to which it is sometimes compared. The vinegar becomes weak and mouldy as these changes go on, and they are rapid in proportion to its weakness.

The vinegar of commerce is very various as to strength, and before the present method of producing it from *pyroligneous acid*, which I shall immediately describe, was brought into practice, it was generally adulterated with other acids, especially the sulphuric, a fraud detected by the production of a precipitate insoluble in nitric acid, on the addition of acetate of baryta. Vinegar is also sometimes sharpened by hydrochloric acid, when it gives a precipitate, likewise insoluble in nitric acid, with nitrate of silver. These precipitates require to be tested, in regard to their insolubility in nitric acid, because they are thus distinguished from other combinations of baryta and of oxide of silver, produced by the other acids or substances present in genuine vinegar; but small traces of sulphuric acid are found in almost all vinegars, and these must be allowed for in using the barytic test. If nitric acid be present in vinegar, it changes the

color of a weak solution of indigo, when boiled with it. Pepper, and other acrid substances, are rendered evident by carefully neutralizing the vinegar with carbonate of soda, when they are detected by their undisguised pungency.

The specific gravity of vinegar depends more upon the foreign matters which it contains, than upon its actual strength, so that its value cannot be judged of by that criterion: the density of the best vinegar (commonly called *white-wine* vinegar), is about 1.020 to 1.025. To ascertain the proportion of *real acetic acid* which it contains, it must be cautiously neutralized by carbonate of soda (dry or crystallized), and the quantity of that salt requisite for the purpose indicates the proportion of real acetic acid present, 54 parts of *dry* carbonate of soda being equivalent to 51 of true or anhydrous acetic acid. The equivalent of *carbonate of lime*, which is 50, is so near that of acetic acid, as to furnish a ready mode of ascertaining the value of vinegar or other dilute acetic acid; for this purpose a piece of clean white marble is selected and accurately weighed. It is then suspended by a thread in a proper quantity of the vinegar to be examined, which is occasionally cautiously stirred, so as to mix its parts without chipping the marble; when it is no longer acted on, it is removed, washed, dried, and weighed; its loss is equivalent to the acetic acid. Another mode of ascertaining the strength of vinegar consists in neutralizing it by hydrate of lime; acetate of lime is extremely soluble, so that the quantity of acetate of lime formed and dissolved, is directly as the quantity of acid present, and the *density* of the resulting solution of acetate of lime, is in the same ratio. (See Messrs. J. and P. TAYLOR on an *Acetometer*. *Quart. Jour.*, vi.) A solution of ammonia, of known strength, blued by litmus, may sometimes conveniently be used as a neutralizing acetometric fluid. "An ounce of good vinegar should saturate about 30 to 32 grains of pure and dry carbonate of potassa; such vinegar contains about 5 *per cent.* of *anhydrous acetic acid*, and its density is from 1.01 to 1.03." (LIEBIG.)

**DISTILLED VINEGAR.** When vinegar is subjected to careful distillation, the first portion which passes over usually contains a little alcohol; this is followed by dilute acetic acid, which, towards the end of the process, especially if distilled over an open fire, acquires an empyreumatic odor: the residue is brown, very acid, and has a burned flavor. According to R. Phillips (on the *London Pharmacopæia*, p. 7), when the best English malt-vinegar, of the specific gravity 1.0204, is distilled, the first eighth part which passes over is of the specific gravity 0.99712, so that it contains a little alcohol; a fluid-ounce of it, = 1.8047 cubic inches, dissolves from 4.5 to 5 grains of precipitated carbonate of lime: the next six-eighths have the specific gravity 1.0023, and a fluid-ounce dissolves 8.12 grains of the carbonate; a fluid-ounce of the acid, of specific gravity 1.007, dissolves 15 to 16 grains of precipitated carbonate of lime, or 13.8 grains of marble.

Distilled vinegar is colorless, and wants the agreeable fresh flavor and odor of the original vinegar, compared with which it is flat: it contains a trace of alcohol and of acetic ether, and also of a peculiar organic matter which passes over in distillation, and which distilled vinegar sometimes deposits in the form of a gray sediment; its nature is unknown: when



the acid containing it is neutralized by an alkali and slowly evaporated, it communicates a brown tinge, in consequence of the action of the air upon it. If vinegar has been distilled from a copper still, through a pewter worm, it is always more or less contaminated by copper, lead, or tin, and consequently becomes discolored when tested by sulphuretted hydrogen, especially after it has been reduced in bulk by evaporation. Earthenware, or even silver condensing-tubes, are therefore used by the wholesale vinegar-distillers; or upon the small scale, glass vessels may be employed; but the use of distilled vinegar is now almost entirely superseded by that of a mixture of pure acetic acid and water, and this mixture, colored by burned sugar, is pretty generally employed as a substitute for vinegar.

When vinegar is subjected to a low temperature its aqueous part is that which first congeals, and the remaining unfrozen portion is the strongest; in this way vinegar may, to a certain extent, be concentrated.

**PYROLIGNEOUS ACID.** The production of *vinegar* by the destructive distillation of wood, was one of the numerous discoveries of Glauber; but a similar acid was probably known at a much more remote period, and used by the Egyptians in the process of mummification. Berzelius quotes the following passage from Pliny in favor of this opinion. (*Hist. Nat.*, lib. xvi., p. 2.) “*Pix liquida in Europa e teda (Pinus silvestris) coquitur, navalibus muniendis, multosque alios ad usus. Lignum ejus concisum, furnis, undique igne extra circumdato, fervet; primus sudor, aquæ modo, fluit canali; hoc, in Syria, cedrum vocatur, cui tanta est vis, ut in Ægypto, corpora hominum defunctorum, eo perfusa, servantur.*” (See also, in reference to this subject, the article *Kreasote*, p. 1215.) The distillation of wood is now carried on upon a large scale, expressly for obtaining the acid. For this purpose the following form of the apparatus is used. A series of cast-iron cylinders, about 4 feet in diameter, and 6 feet long, are built horizontally in brick-work, so that the flame of one furnace may play round about two cylinders, both ends of which project a little from the brick-work. One of them has a disc of cast iron well fitted and firmly bolted to it, from the centre of which disc an iron tube about 6 inches diameter proceeds, and enters at a right angle the *main* tube of refrigeration. The diameter of this tube may be from 9 to 14 inches, according to the number of cylinders. The other end of the cylinder is called the mouth of the retort. This is closed by a disc of iron, smeared round its edge with clay-lute, and secured in its place by wedges. The charge of wood for such a cylinder is about 8 cwt. (See the similar apparatus described at p. 1211.) The hard woods, oak, ash, birch, and beech, are alone used, and these should be *seasoned* or kept for some time to become dry. Fir does not answer\*. The heat is kept up during the day-time, and the furnace is allowed to cool during the night. Next morning the mouth is opened, the charcoal removed, and a new charge of wood is introduced. The average produce of crude vinegar, called *pyroligneous acid*, is 35 gallons. It is much contaminated with tar;

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\* In reference to this subject, it appears from Stoltze's experiments, that the dried wood of all trees yields nearly the same quantity of fluid product when similarly dis-

is of a deep-brown color; and has a specific gravity of 1·025. Its total weight is therefore about 300 lbs. But the residuary charcoal is found to weigh no more than one-fifth of the wood employed. The crude pyroligneous acid is rectified by a second distillation in a copper still, in the body of which about 20 gallons of viscid tarry matter are left from every 100. It has now become a transparent brown vinegar, having a considerable empyreumatic smell, and a specific gravity of 1·013. Its acid powers are superior to those of the best household vinegar, in the proportion of 3 to 2. (URE's *Dictionary*, Art. ACID, *acetic*.)

The purification of this crude acid is generally effected as follows: it is saturated with slaked lime, previously made into a thin cream with water; in this way much of the empyreumatic extractive is precipitated in insoluble combination with the lime; the clear solution, containing acetate of lime, is then drawn off and mixed with a concentrated solution of sulphate of soda, till no further precipitation of sulphate of lime ensues; when this has fallen, the supernatant liquor is let off, the residuary sulphate washed, and the whole of the solution evaporated; during this process, empyreumatic resin separates upon the surface, and is skimmed off, and when the solution has acquired a due density, it is set aside to crystallize, and the mother-liquor is poured off and treated as before. At last, a brown uncrystallizable liquid remains, which contains, besides acetate of soda, an empyreumatic extractive, and resin combined with soda, and which may be decomposed by evaporation to dryness, and calcination, so as to leave the soda. The crystallized salt, which is impure acetate of soda, after having been purified by solution and recrystallization, is fused in an iron pot, stirred till it dries, and the heat is then carefully raised to incipient carbonization, by which the empyreumatic matters which rendered it impure are carbonized, whilst the salt itself, if the operation be skilfully conducted, is little damaged; the mass is then dissolved in water, filtered, and recrystallized, and yields pure *acetate of soda*. This salt is then distilled with 0·36 of its weight of sulphuric acid, either in glass, or in metallic stills with silver condensers. The product is a strong acid, of the specific gravity 1·05; it still has an empyreumatic flavor, which is removed by well-burned animal charcoal; it is then duly diluted with water, and applicable to all the purposes for which common vinegar is employed; when intended for the table, it is colored by burned sugar, and flavored by a few drops of acetic ether. For

tilled, but that the proportion of acetic acid in it is very variable. The following table illustrates this:—

| 100 parts of dry wood yield                 | Acid<br>Liquor. | 1 ounce of<br>which saturates<br>grains of<br>Carbonate of<br>Potassa. | Empyreumatic<br>Oil. | Charcoal. |
|---|-----------------|--|----------------------|-----------|
| Birch, ( <i>Betula alba</i> ) .....         | 45              | 55   | 8·60                 | 24·4      |
| Beech, ( <i>Fagus sylvatica</i> ).....      | 44              | 54   | 9·55                 | 24·6      |
| Oak, ( <i>Quercus robur</i> ) .....         | 43              | 50   | 9·06                 | 26·2      |
| Ash, ( <i>Fraxinus excelsior</i> ) .....    | 46·8            | 44   | 8·80                 | 22·1      |
| White poplar, ( <i>Populus alba</i> )       | 45·8            | 39   | 8·05                 | 23·4      |
| Wild plum, ( <i>Prunus padus</i> ) ....     | 43·7            | 37   | 10·35                | 21·6      |
| Juniper, ( <i>Juniperus communis</i> )      | 45·8            | 29   | 10·73                | 22·7      |
| Spruce fir, ( <i>Pinus abies</i> ) .....    | 41·2            | 29   | 13·70                | 21·2      |
| Scotch fir, ( <i>Pinus sylvestris</i> ).... | 42·4            | 28   | 11·80                | 21·5      |



pickles and sauces of all kinds, it is generally used in a somewhat stronger state than common vinegar. It is used as a substitute for vinegar in all the processes of the arts, being more or less purified in these cases, according to the purposes for which it is required.

CONCENTRATED ACETIC ACID,  $C_4 H_3 O_3 + HO$ , ( $= AcO_3, HO$ ). This acid, the composition of which has been above given, (p. 1711), is obtained by decomposing *acetate of soda*; this salt is first purified by two or three solutions and crystallizations, and then carefully desiccated, by heating and stirring it, without fusion, in an iron basin; it is then pulverized, and put into a capacious tubulated retort, with two equivalents of pure sulphuric acid, at a temperature of about  $125^\circ$ ; acetic acid is liberated, but when about an eighth part has passed over, the retort must be carefully heated; the distillation may be continued till the saline matter in the retort, which is bisulphate of soda, is in quiet fusion. The product of this first distillation must be rectified over a little dried acetate of soda, and then placed in ice till it congeals; the congealed acid is suffered to drain, by inverting the bottle which contains it, and in that frozen state it may be regarded as *pure hydrated acetic acid*; it retains its solid form till the thermometer rises to about  $50^\circ$ ; if cooled down to  $45^\circ$ , and then shaken, or a particle of solid matter dropped into it, it congeals, and at the same time an immersed thermometer rises to  $51^\circ$ . This crystallization of acetic acid seems to have been first noticed by the Marquis de Courtanvaux, in 1768. (*Mém. de l'Académie*, v. 72.) Its crystals are generally flat plates of a pearly lustre; it has a strong irritating odor, agreeable when much diluted, and is powerfully acid and caustic, reddening the skin, and raising a blister. It absorbs moisture from the air, and dissolves in all proportions in water, and in alcohol. The specific gravity of this acid (the liquified crystallized acid) is 1.06296 at  $60^\circ$ ; but its density is no criterion of its strength, as shown in the following table, drawn up by Dr. Thomson:

| Atoms of<br>Acid. |   | Atoms of<br>Water. |       | Sp. Gr.<br>at $60^\circ$ . | Atoms of<br>Acid. |   | Atoms of<br>Water. |       | Sp. Gr.<br>at $60^\circ$ . |
|-------------------|---|--------------------|-------|----------------------------|-------------------|---|--------------------|-------|----------------------------|
| 1                 | + | 1                  | ..... | 1.06296                    | 1                 | + | 6                  | ..... | 1.06708                    |
| 1                 | + | 2                  | ..... | 1.07060                    | 1                 | + | 7                  | ..... | 1.06349                    |
| 1                 | + | 3                  | ..... | 1.07084                    | 1                 | + | 8                  | ..... | 1.05974                    |
| 1                 | + | 4                  | ..... | 1.07132                    | 1                 | + | 9                  | ..... | 1.05794                    |
| 1                 | + | 5                  | ..... | 1.06820                    | 1                 | + | 10                 | ..... | 1.05439                    |

The liquid acid, therefore, is at its greatest density when it consists of 1 atom of anhydrous acid, and 4 atoms of water; or of about 100 of real acid and 72 of water. It appears, also, that the density of the *glacial acid*, containing only 1 atom of water, is nearly the same with that containing 7 atoms.

Acetic acid has not been obtained in an uncombined anhydrous state. When heated, it distils over without change. It is only partially decomposed by a red heat, yielding *acetone* and carbonic acid; (LIEBIG and PELOUZE, *Ann. der Pharm.*, xix. 286;) at a very high temperature it is resolved into inflammable gases and carbon. If passed over red-hot charcoal, it yields carbonic acid, water, carbonic oxide, and carburetted hydrogen. When the vapor of acetic acid is passed over platinum-black heated to  $430^\circ$ , it is entirely decomposed. A mixture of 1 part of crystallized

acetate of soda, with 3 or 4 of caustic baryta, is resolved by heat into carbonate of soda, and fire-damp. (REINSCH. MILLON. DUMAS. PELOUZE.)

Cold acetic acid is uninflamable, but when heated, its vapor burns with a blue flame. The oxyacids are almost without action upon it. Chlorine, under ordinary circumstances, little affects it; but exposed to it under the direct solar rays, hydrochloric and chlorocarbonic acids are formed, and crystalline *chloracetic acid*. With anhydrous sulphuric acid it forms a compound, termed by Melsen *sulphacetic acid*, which forms *sulphacetates* with two equivalents of base. (*Chem. Gaz.*, Sept. 1843.) Acetic acid is difficultly decomposed by oxidizement. When it is distilled with binoxide of manganese and dilute sulphuric acid, *formic acid* passes over.

*Acetates*. These salts are mostly *neutral*, the oxygen in the acid being to that in the base as 3 to 1; but with ammonia and potassa it also forms *acid* salts; and with the oxides of lead and copper, *basic* salts. Most of the acetates retain water of crystallization. They are almost all very soluble: there are, perhaps, two exceptions, in those of molybdenum and of tungsten; the acetate of silver, and of black oxide of mercury, are also difficultly soluble. The acetates are decomposed by heat, and yield variable products; those of the alkaline bases yield carbonates, carbonic acid, carbonic oxide, a little carburetted hydrogen, a small quantity of water and of oil, and *pyroacetic spirit*, or *acetone*. Some of the acetates yield acetic acid scarcely altered; and some, a mixture of acid and acetone, leaving charcoal, and the metal or its oxide. The fusible acetates concrete, on cooling, into foliated masses. When acetates are in dilute aqueous solution, they often suffer spontaneous decomposition; some of them become carbonates, and a green mould forms upon their surface. Acetates are recognised by the evolution of acetic acid when acted on by sulphuric acid; and many of them yield a precipitate of nacreous crystalline scales, with a solution of nitrate of suboxide of mercury.

*Acetate of Ammonia*.  $\text{NH}_4\text{O}, \text{AcO}_3$ . In solution, as obtained by saturating distilled vinegar with carbonate of ammonia, this salt constitutes the *liquor ammoniæ acetatis* of the *Pharmacopœia*, which has long been used in medicine as a diaphoretic, under the name of *spirit of Minde-rerus*. When equal weights of acetate of potassa and sal-ammoniac are distilled together, ammonia is evolved, and *binacetate of ammonia* distils over, in the form of an oily liquid, which concretes into acicular crystals, deliquescent, and soluble in alcohol. By passing dry ammonia into the fused binacetate, it is converted into solid neutral acetate, which is a white inodorous salt, readily soluble in water and alcohol, and which is converted by heat into ammonia and *binacetate*. When solution of neutral acetate of ammonia is evaporated *in vacuo* over sulphuric acid, it yields delicate prisms, which slightly redden litmus; they are very deliquescent, and consist, according to Thomson, of  $\text{NH}_4\text{O}, \text{AcO}_3, 6\text{HO}$ . (*First Principles of Chem.*, ii. 250.) The formula of the *binacetate* is probably  $\text{NH}_4\text{O}, \text{HO}, 2\text{AcO}_3$ : it forms striated prisms, fusible at  $168^\circ$ , and subliming unchanged at  $248^\circ$ .

*Acetate of Potassa*,  $\text{KO}, \text{AcO}_3$ , is usually formed by saturating distilled vinegar with carbonate of potassa, and evaporating to dryness. It



is best obtained by saturating pure acetic acid, diluted with 2 or 3 parts of water, with the alkaline carbonate. If this salt be carefully fused, it concretes into a lamellar deliquescent mass on cooling. It is the *terra foliata tartari*, and *febrifuge salt of Sylvius*, of old pharmacy. It dissolves in its own weight of water at 60°, and the solution has a pungent and sweetish saline taste. Boiling alcohol dissolves twice its weight. When chlorine is passed through the aqueous solution of this salt, carbonic acid is evolved, and a powerful bleaching-liquid formed; exposed to air, it gives out chlorine; distilled, it yields acetic acid, a little chlorine, and no oxygen. Carbonic acid decomposes the alcoholic solution of acetate of potassa, carbonate of potassa is deposited, and acetic acid, which produces acetic ether, is set free. Acetate of potassa exists in the sap of several plants, which, when burned, yield carbonate of potassa. In its anhydrous state this salt consists of

|                         |   |     |    |     |       | Wenzel. | Richter. |       |       |
|-------------------------|---|-----|----|-----|-------|---------|----------|-------|-------|
| Potassa .....           | 1 | ... | 48 | ... | 48·5  | ...     | 50·15    | ...   | 51·4  |
| Acetic acid .....       | 1 | ... | 51 | ... | 51·5  | ...     | 49·85    | ...   | 48·6  |
| <hr/>                   |   |     |    |     |       | <hr/>   | <hr/>    | <hr/> | <hr/> |
| Acetate of potassa .... | 1 |     | 99 |     | 100·0 |         | 100·00   |       | 100·0 |

*Binacetate of Potassa.* KO,HO,2AcO<sub>3</sub>. This salt is formed, according to Melsens, (*Ann. der Pharm.*, xliv. 97,) by slowly evaporating a solution of the neutral acetate mixed with excess of acetic acid: it forms flexible prisms, which slowly deliquesce in the air; their hot concentrated alcoholic solution concretes on cooling. This salt may be heated to 250° without decomposition. The crystals fuse at 298°, and at about 390° are resolved into acetic acid and neutral acetate: at about 570°, the latter salt is decomposed.

*Acetate of Soda.* NaO, AcO<sub>3</sub>. This is an easily-crystallizable salt; its forms are very complex, and are derived from an oblique rhombic prism. (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 39.) When it contains a little tar, the crystals are often bulky. They effloresce in dry air; they are soluble in 3 parts of cold, and less of boiling water; and in 5 parts of alcohol. This salt has a saline, but not disagreeable flavor: it fuses when heated, and concretes into a lamellar mass, formerly called *terra foliata mineralis*: it may be heated up to 600°, without suffering decomposition. It is of importance, as above stated, as a source of *acetic acid*. At a red heat it leaves a mixture of carbonate of soda and carbon, in a favorable state for the preparation of sodium (see p. 605). The *anhydrous* salt consists of

|                               |   |     |    |     |       | Berzelius. | Wenzel. |       |        |
|-------------------------------|---|-----|----|-----|-------|------------|---------|-------|--------|
| Soda .....                    | 1 | ... | 32 | ... | 38·5  | ...        | 38·311  | ...   | 39·67  |
| Acetic acid .....             | 1 | ... | 51 | ... | 61·5  | ...        | 61·689  | ...   | 60·33  |
| <hr/>                         |   |     |    |     |       | <hr/>      | <hr/>   | <hr/> | <hr/>  |
| Anhydrous acetate of soda.... | 1 |     | 83 |     | 100·0 |            | 100·000 |       | 100·00 |

The crystallized salt, KO, AcO<sub>3</sub>, 6HO, contains

|                              |     |     |       |     |       |     | Thomson and Berzelius. |
|------------------------------|-----|-----|-------|-----|-------|-----|------------------------|
| Soda .....                   | 1   | ... | 32    | ... | 23·4  | ... | 22·94                  |
| Acetic acid .....            | 1   | ... | 51    | ... | 37·2  | ... | 36·95                  |
| Water .....                  | 6   | ... | 54    | ... | 39·4  | ... | 40·11                  |
| <hr/>                        |     |     | <hr/> |     | <hr/> |     | <hr/>                  |
| Crystallized acetate of soda | ... | 1   | 137   |     | 100·0 |     | 100·00                 |

*Acetate of Lithia*,  $\text{LiO}, \text{AcO}_3$ , is a very deliquescent and difficultly-crystallizable salt.

*Acetate of Lime*,  $\text{CaO}, \text{AcO}_3$ , forms silky acicular prisms of a bitterish saline taste, which effloresce when heated to  $212^\circ$ , and are soluble in water and alcohol; this salt is used in the formation of acetate of soda in the process for procuring acetic acid; when heated to  $226^\circ$ , and triturated, it is phosphorescent in the dark. It consists, in its *anhydrous* state, of

|                      |   |     |    |     |       | Berzelius. | Higgins. | Richter. |       |     |       |
|----------------------|---|-----|----|-----|-------|------------|----------|----------|-------|-----|-------|
| Lime .....           | 1 | ... | 28 | ... | 35.4  | ...        | 35.4     | ...      | 35.7  | ... | 34.3  |
| Acetic acid .....    | 1 | ... | 51 | ... | 64.6  | ...        | 64.6     | ...      | 64.3  | ... | 65.7  |
| <hr/>                |   |     |    |     |       |            |          |          |       |     |       |
| Acetate of lime .... | 1 |     | 79 |     | 100.0 |            | 10.00    |          | 100.0 |     | 100.0 |

*Acetate of Baryta*,  $\text{BaO}, \text{AcO}_3$ , is formed by digesting sulphuret of barium, or carbonate of baryta, in acetic acid, filtering, and evaporating; dried at  $212^\circ$ , it yields a white powder, soluble in about its weight of water, sparingly soluble in alcohol, and of an acrid pungent taste: when crystallized at a temperature below  $60^\circ$ , it includes, according to Mitscherlich, 3 atoms of water, and its form resembles that of acetate of lead; above  $60^\circ$  it forms crystals with 1 atom of water, which are irregular six-sided prisms, terminated by dihedral summits, the primary form of which is a right rhomboidal prism. (BROOKE, *Ann. of Phil.*, 2nd Series, vii. 365.) In cold weather the concentrated solution concretes into a congeries of silky crystals. It is sometimes used as a test of sulphuric acid. The *anhydrous* salt consists of

|                             |   |     |     |     |       |     | Bucholz. | Richter. |       |
|-----------------------------|---|-----|-----|-----|-------|-----|----------|----------|-------|
| Baryta .....                | 1 | ... | 77  | ... | 60.2  | ... | 60.56    | ...      | 59.4  |
| Acetic acid .....           | 1 | ... | 51  | ... | 39.8  | ... | 39.44    | ...      | 40.6  |
| <hr/>                       |   |     |     |     |       |     |          |          |       |
| Anhydrous acetate of baryta | 1 |     | 128 |     | 100.0 |     | 100.00   |          | 100.0 |

and the common *crystallized* acetate contains

|                                    |   |      |     |      |       |      | Bucholz. |
|------------------------------------|---|------|-----|------|-------|------|----------|
| Baryta .....                       | 1 | .... | 77  | .... | 56.2  | .... | 56.70    |
| Acetic acid .....                  | 1 | .... | 51  | .... | 37.2  | .... | 36.93    |
| Water .....                        | 1 | .... | 9   | .... | 6.6   | .... | 6.37     |
| <hr/>                              |   |      |     |      |       |      |          |
| Crystallized acetate of baryta.... | 1 |      | 137 |      | 100.0 |      | 100.00   |

*Acetate of Strontia*,  $\text{SrO}, \text{AcO}_3$ , is soluble in 2.5 parts of water, at  $60^\circ$ ; the ordinary crystals include 1 atom of water. (THOMSON.) The crystals formed below  $60^\circ$  contain 4 atoms of water. According to Löwig, the crystals formed above  $60^\circ$  are  $2[\text{SrO}, \text{AcO}_3] + \text{HO}$ .

*Acetate of Magnesia*,  $\text{MgO}, \text{AcO}_3$ , is a very difficultly crystallizable bitter salt; it is generally obtained in the form of a gum-like mass, slightly deliquescent, soluble in water and alcohol, and composed of

|                     |   |       |    |       |        | Richter.   |
|---------------------|---|-------|----|-------|--------|------------|
| Magnesia .....      | 1 | ..... | 20 | ..... | 28.17  | ..... 28.9 |
| Acetic acid .....   | 1 | ..... | 51 | ..... | 71.83  | ..... 71.1 |
| <hr/>               |   |       |    |       | <hr/>  | <hr/>      |
| Acetate of magnesia | 1 |       |    |       | 100.00 | 100.0      |



*Acetate of Manganese.*  $\text{MnO}, \text{AcO}_3$ . This salt is prepared for the use of calico-printers by mixing sulphate of manganese with acetate of lime. It forms transparent pale-red rhomboidal tables, soluble in water and alcohol. When printed upon calico and passed through a bath of chloride of lime, a brown oxide of manganese is formed upon the fibre.

*Protacetate of Iron.*  $\text{FeO}, \text{AcO}_3$ . This salt is obtained by the action of acetic acid on protosulphuret of iron: it forms a mass of white silky crystals when evaporated out of contact of air. When iron filings are digested in acetic acid, the resulting solution contains a mixture of peracetate and protacetate. When acetate of baryta or acetate of lead, and protosulphate of iron, are mixed in atomic proportions, double decomposition ensues, and protacetate of iron and sulphate of baryta or of lead are the results.

*Peracetate of Iron,*  $\text{Fe}_2\text{O}_3, 3\text{AcO}_3$ , may be obtained by digesting turnings and clippings of iron in acetic acid exposed to air; or by dissolving hydrated peroxide of iron in the acid; or by mixing acetate of lead or of baryta with persulphate of iron: it forms a deep reddish-brown solution, which, when carefully concentrated, yields a gelatinous residue, but does not crystallize; if rapidly evaporated, it deposits a yellow powder, which is said to be a *diacetate*. This solution is much employed by dyers and calico-printers.

*Acetate of Zinc,*  $\text{ZnO}, \text{AcO}_3$ , is formed either by dissolving oxide of zinc in acetic acid, or by mixing a solution of sulphate of zinc with one of acetate of lead. It crystallizes in thin shining rhomboidal plates, of a bitter and metallic taste, very soluble, but not deliquescent: their primary form is an oblique rhombic prism. (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 39.) This salt is sometimes used in pharmacy, chiefly as an external application. According to Messrs. Aikin, the specific gravity of a saturated solution of acetate of zinc, made by digesting the metal in distilled vinegar, is 1.055. Of this solution, 900 grains contain 53 of dry, or 82.6 of crystallized acetate. One ounce, by measure, of the solution, weighs 506 grains, and contains 29.8 grains of dry, or 46.5 grains of crystallized salt. This salt, in its usual crystallized form, includes, according to Thomson, 7 atoms of water; but it also crystallizes with 3 atoms. When acetate of zinc is highly heated, it yields, according to Völckel, a woolly sublimate of an acid acetate.

*Acetate of Tin.* This metal is slowly acted on by acetic acid, but a *protacetate* and *peracetate of tin* may be made by mixing acetate of lead with saturated solutions of the protochloride and perchloride of tin. These solutions have been recommended as mordants for the use of dyers. The protacetate is crystallizable. Vinegar, kept in tin vessels, dissolves a very minute portion of the metal; and in pewter vessels, it likewise dissolves a small portion of the lead, where in contact both with the vinegar and air; hence, distilled vinegar, which has been condensed in a pewter worm, affords generally traces of both metals. (VAUQUELIN, *Ann. de Ch.*, xxxii.)

*Acetate of Cadmium.*  $\text{CdO}, \text{AcO}_3$ . When a concentrated solution of this salt is exposed for about ten days to the air, it is gradually converted into a crystalline mass, while a dense liquid remains above it. The

crystals are prisms, very soluble in water, and not altered by exposure to air: they include 2 atoms of water. (THOMSON.)

*Acetate of Cobalt.*  $\text{CoO}, \text{AcO}_3$ . Oxide of cobalt is easily soluble in acetic acid, forming a red solution; it yields a red deliquescent salt when carefully evaporated, becoming blue when heated, and forming a good sympathetic ink. (ILSEMANN, *Crell's Annals*, 1785, ii. 25.)

*Acetate of Nickel.*  $\text{NiO}, \text{AcO}_3$ . Carbonate of nickel dissolves readily in acetic acid, forming a dark-green solution, from which rhomboidal crystals may be obtained, soluble in water, but insoluble in alcohol; when heated, they give out water and become yellow, then burn like tinder, and leave oxide of nickel: they include 5 atoms of water. (THOMSON.) Acetate of nickel is soluble in 6 parts of cold water, and insoluble in absolute alcohol.

*Acetate of Copper.*  $\text{CuO}, \text{AcO}_3$ . This salt is generally distinguished as *crystallized verdigris*\*; it has been long known, and is described by Pliny (lib. xxxiv., c. ii.) It is prepared by dissolving the *subacetate* or *common verdigris* in acetic acid; the solution is put into pans, and allowed slowly to crystallize, generally upon twigs, or pieces of string suspended in it: it forms oblique rhombic prisms (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 39), of a rich blueish-green color, soluble in 5 parts of boiling water, and sparingly soluble in alcohol. The dilute aqueous solution is decomposed when boiled, and deposits a tribasic salt. When this salt is heated in the air, it burns with a green flame; submitted to destructive distillation, it yields water, acetic acid, acetone, carburetted gases, and a white crystalline sublimate, which is an *acetate of the suboxide of copper*,  $= \text{Cu}_2\text{O}, \text{AcO}_3$ , and which, when dissolved in water soon passes into common acetate, and deposits metallic copper: the residue consists of very finely-divided copper mixed with a little charcoal, which is pyrophoric, and burns like tinder when heated. This salt was formerly a principal source of strong acetic acid, but since the discovery of the modes of purifying and concentrating pyroligneous acid, it has fallen into disuse. When sugar is added to a boiling solution of acetate of copper, a red crystalline powder (suboxide of copper) falls, and the remaining filtered solution contains some peculiar combination of copper, which has not been accurately examined. This salt, when crystallized at temperatures below  $50^\circ$ , sometimes forms oblique 4-sided prisms, which include 5 atoms of water, and which when heated to  $86^\circ$  crack into small crystals of the ordinary monohydrated salt, giving off 4 atoms of water. When sulphate, nitrate, or chloride of copper, is dissolved in strong liquid ammonia with the aid of heat, until neutral, and excess of acetic acid added and boiled, minute crystals of neutral acetate of copper form upon the surface, and are deposited in considerable quantity when the solution is stirred. (JONAS. *Chem. Gaz.*, Sept., 1843.) When saturated solutions of neutral acetate of copper and corrosive sublimate are mixed, clusters of radiating crystals are soon deposited, almost insoluble in cold water, and decomposed by boiling water: their formula is  $(2\text{CuO}, \text{AcO}_3) + 2\text{Hg Cl}$ . (WÖHLER.)

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\* There are three commercial varieties of verdigris: the *crystallized* or neutral acetate; the *blue* or subacetate; and the *green*, which is a mixture of the sesqui and tribasic acetates.



The components of acetate of copper in its ordinary crystalline state, are

|                                |   |     |     | Phillips. | Ure.  | Gehlen. | Berzelius. |
|--------------------------------|---|-----|-----|-----------|-------|---------|------------|
| Oxide of copper .....          | 1 | ... | 40  | ...       | 39.2  | ...     | 39.29      |
| Acetic acid .....              | 1 | ... | 51  | ...       | 49.9  | ...     | 52.0       |
| Water .....                    | 1 | ... | 9   | ...       | 10.9  | ...     | 8.4        |
|                                |   |     |     |           |       |         |            |
| Crystallized acetate of copper | 1 |     | 100 |           | 100.0 |         | 100.00     |

*Diacetate of Copper. Subacetate of Copper.*  $2\text{CuO}, \text{AcO}_3, + 6\text{HO}$ . This dibasic salt is the *verdigris* or *ærugo* of commerce; it is prepared by exposing thin plates of copper to the action of acetic acid, or its fumes; the method now practised consists in alternating plates of copper with pieces of woollen cloth steeped in acetic acid; they gradually become corroded and superficially covered with verdigris, which is from time to time removed, in the form of a blue-green powder, and the operation repeated as long as the plate lasts. Sometimes the husks and stalks of grapes or raisins, in a state of acetous fermentation, are employed to act upon the copper, as is the case with some of the French verdigris. This article is commonly rolled or packed in white leather, and is frequently much adulterated with a mixture of chalk and sulphate of copper. Pure diacetate of copper forms small silky crystals of a greenish-blue color, which, when heated to  $212^\circ$ , become green, and lose water; when moistened a little, this salt crumbles, and is only partially soluble in water, by which it is ultimately resolved into *tribasic*, and *neutral* acetate. This salt consists of

|                                    |   |     |     |     | Berzelius. |
|------------------------------------|---|-----|-----|-----|------------|
| Oxide of copper .....              | 2 | ... | 80  | ... | 43.24      |
| Acetic acid .....                  | 1 | ... | 51  | ... | 27.57      |
| Water .....                        | 6 | ... | 54  | ... | 29.19      |
|                                    |   |     |     |     |            |
| Hydrated diacetate of copper ..... | 1 |     | 185 |     | 100.00     |

Phillips has given the following comparative statement of the composition of the different kinds of verdigris. (*Ann. of Phil.*, 2nd Series, vi. 39.)

|                          | Blue Crystals. | French Verdigris. | English Verdigris. |
|--------------------------|----------------|-------------------|--------------------|
| Acetic acid .....        | 28.30          | ...               | 29.3               |
| Peroxide of copper ..... | 43.25          | ...               | 43.5               |
| Water .....              | 28.45          | ...               | 25.2               |
| Impurity .....           | ...            | ...               | 2.0                |
|                          |                |                   |                    |
|                          | 100.00         |                   | 100.0              |

*Subsesquiacetate of Copper.*  $3\text{CuO}, 2\text{AcO}_3, + 6\text{HO}$ . This sesqui-basic salt is obtained by triturating the diacetate with water, filtering the solution, concentrating it by slow evaporation, heating so as to dissolve the deposit, and then adding alcohol; when the solution is set aside, a gelatinous mass of minute crystals is formed, which when dry are of a pale blue color, and consist of

|   |   |     |     |     | Berzelius. |
|---|---|-----|-----|-----|------------|
| Oxide of copper .....                   | 3 | ... | 120 | ... | 43.48      |
| Acetic acid .....                       | 2 | ... | 102 | ... | 36.96      |
| Water .....                             | 6 | ... | 54  | ... | 19.56      |
|   |   |     |     |     |            |
| Crystallized subsesquiacetate of copper | 1 |     | 276 |     | 100.00     |

When this sesquiacetate,  $= 3\text{CuO}, 2\text{AcO}_3$ , is digested in boiling water, a brown flocculent precipitate is formed, composed, according to Berzelius, of  $48\text{CuO}, \text{AcO}_3, + 2\text{H}_2\text{O}$ ; but the existence of this, as a definite compound, seems doubtful.

*Trisacetate of Copper.*  $3\text{CuO}, \text{AcO}_3$ . This tribasic salt is the portion of the *diacetate* which is insoluble in water, and which, when thoroughly washed with alcohol, and dried at  $212^\circ$ , consists of

|                                     |   |     |     |     |       | Berzelius. |        |
|-------------------------------------|---|-----|-----|-----|-------|------------|--------|
| Oxide of copper .....               | 3 | ... | 120 | ... | 63.5  | ...        | 64.36  |
| Acetic acid .....                   | 1 | ... | 51  | ... | 27.0  | ...        | 27.60  |
| Water .....                         | 2 | ... | 18  | ... | 9.5   | ...        | 8.04   |
| <hr/>                               |   |     |     |     |       |            |        |
| Hydrated trisacetate of copper .... | 1 |     | 189 |     | 100.0 |            | 100.00 |

The *common verdigris* of commerce is no doubt a mixture of two or more, of the preceding acetates; the common green varieties are generally resolvable by water into  $\text{CuO}, \text{AcO}_3$ , and  $3\text{CuO}, 2\text{AcO}_3$ ; the *blue verdigris*, made by exposing plates of copper to the action of the neutral acetate of copper, and which is above represented as  $2\text{CuO}, \text{AcO}_3, 6\text{H}_2\text{O}$ , may be resolved by water into  $\text{CuO}, \text{AcO}_3$ , and  $3\text{CuO}, \text{AcO}_3$ . There are therefore probably 4 *basic* acetates and one *neutral* salt; namely, (1.)  $48\text{CuO}, \text{AcO}_3$ . (2.)  $3\text{CuO}, \text{AcO}_3$ . (3.)  $2\text{CuO}, \text{AcO}_3$ . (4.)  $3\text{CuO}, 2\text{AcO}_3$ . (5.)  $\text{CuO}, \text{AcO}_3$ .

*Acetate of Lead.*  $\text{PbO}, \text{AcO}_3 + 3\text{H}_2\text{O}$ . Oxide of lead combines, like oxide of copper, in several proportions with acetic acid. The *neutral acetate* has long been known under the name of *sugar of lead*; it is the *salt of Saturn* of the old chemists, and is a considerable article of commerce, being much used in various operations connected with dyeing and calico-printing. It is prepared by digesting oxide of lead in pyroligneous acid, or in pure dilute acetic acid, taking care to avoid excess of the oxide. It is found, in trade, of various degrees of purity, according to the purposes for which it is intended. When plates of lead are exposed to the fumes of vinegar or acetic acid, they become corroded, and incrustated with a mixture of acetate and carbonate of lead, and which, scraped off and dissolved in excess of acetic acid, forms a solution from which crystallized acetate of lead is also obtained by evaporation. This salt crystallizes in acicular masses, when its hot concentrated solution is set aside to cool, and in this state it is generally found in commerce; by slower evaporation, it yields truncated and flattened quadrangular and hexahedral prisms, cleavable parallel to the lateral and terminal planes of a right rhombic prism, which may be considered as its primary form. (BROOKE, *Ann. of Phil.*, 2nd Series, vi. 374.) These crystals are permanent in ordinary states of the atmosphere, but they effloresce, and ultimately become anhydrous, at about  $100^\circ$ , *in vacuo* over sulphuric acid; they also gradually become anhydrous in the atmosphere, at a temperature between  $70^\circ$  and  $80^\circ$ . The anhydrous acetate is soluble in boiling absolute alcohol, and on slow cooling is deposited in hexagonal tables. Acetate of lead has a singularly sweet, and somewhat astringent, taste: its sp. gr. is 2.57. It exhibits an alkaline reaction upon the blue of violets, even in the presence of excess of acetic acid. Water boiled upon it dissolves 0.29, and retains, when cold, 0.27 of its weight.



(BOSTOCK.) According to Payen (*Ann. Ch. et Ph.*, LXVI. 42) 100 parts of water at  $60^{\circ}$ , dissolve 59 parts of the crystals. It does not raise the boiling-point of water. It dissolves, in its ordinary state, in about 8 parts of alcohol. When heated, the crystals fuse at about  $130^{\circ}$ ; at  $212^{\circ}$  the liquid salt boils, and having lost its water of crystallization, concretes into a lamellar mass; at a higher temperature, this fuses, then gives out acetic acid, acetone, and carbonic acid, and the residue of its destructive distillation is charcoal, and very finely-divided lead, in a highly combustible or pyrophoric state. A brown, or impure sugar of lead, made by digesting litharge in rough pyroligneous acid, is manufactured expressly for the use of dyers.

Acetate of lead is partially decomposed by carbonic acid, which throws down a portion of carbonate of lead, and the acetic acid which is set free protects the remaining solution from further precipitation; the carbonic acid contained in the atmosphere partially decomposes acetate of lead in this way. All the acids and their salts, which form insoluble or difficultly soluble compounds with oxide of lead, also decompose this salt, and these are very numerous; and in consequence of the facility with which the insoluble salts of lead are decomposed, when diffused through water, by sulphuretted hydrogen, such applications of the acetate are of frequent occurrence. The fixed alkalis throw down hydrated oxide of lead from the solution of the acetate, but pure ammonia does not at first precipitate the cold aqueous solution, but forms a precipitate of oxide of lead when boiled. Excess of the fixed alkalis redissolve the oxide. The *anhydrous* acetate consists of

|                                |   |     |     |     |        | Berzelius. |        |
|--------------------------------|---|-----|-----|-----|--------|------------|--------|
| Oxide of lead .....            | 1 | ... | 112 | ... | 68·71  | ...        | 68·52  |
| Acetic acid .....              | 1 | ... | 51  | ... | 31·29  | ...        | 31·48  |
| <hr/>                          |   |     |     |     |        |            |        |
| Anhydrous acetate of lead .... | 1 |     | 163 |     | 100·00 |            | 100·00 |

The components of the *crystallized* salt are

| Berzelius. Thenard.                     |   |     |     |     |        |     |        |     |     |   |
|---|---|-----|-----|-----|--------|-----|--------|-----|-----|---|
| Oxide of lead ... ..                    | 1 | ... | 112 | ... | 58.95  | ... | 58.71  | ... | 58  | } = {<br>Anhydrous }<br>acetate.... }<br>Water .... } |
| Acetic acid .....                       | 1 | ... | 51  | ... | 26.84  | ... | 26.97  | ... | 26  |   |
| Water.....                              | 3 | ... | 27  | ... | 14.21  | ... | 14.32  | ... | 16  |   |
| <hr/>                                   |   |     |     |     |        |     |        |     |     |   |
| Crystallized ace-<br>tate of lead ....} | 1 |     | 190 |     | 100.00 |     | 100.00 |     | 100 | 1 190 100.00  |

*Sesquibasic Acetate of Lead.*  $3\text{PbO}, 2\text{AcO}_3$ . This salt is obtained in the form of pearly six-sided scales, soluble in water and alcohol, by fusing the neutral acetate till it forms a white spongy mass, the solution of which is then evaporated to the consistence of syrup, and set aside to crystallize. (WÖHLER, *Ann. der Pharm.*, XXIX. 64.)

*Diacetate of Lead.*  $2\text{PbO}, \text{AcO}_3$ . This salt is formed, according to Thomson, (*First Principles of Chem.*, II. 373,) by boiling a solution of the neutral acetate with the requisite atomic proportion of litharge: on evaporation, it falls as a white crystalline sediment, of a sweet astringent taste, and soluble in water. Its constituents, when dried by pressure in bibulous paper till it ceases to give out moisture, are

|                                 |    |      |     |      |          |
|---------------------------------|----|------|-----|------|----------|
|                                 |    |      |     |      | Thomson. |
| Oxide of lead .....             | 2  | .... | 224 | .... | 61.2     |
| Acetic acid .....               | 1  | .... | 51  | .... | 14.0     |
| Water .....                     | 10 | .... | 90  | .... | 24.8     |
| <hr/>                           |    |      |     |      | <hr/>    |
| Hydrated diacetate of lead..... | 1  |      | 365 |      | 100.0    |

*Trisacetate of Lead.*  $3\text{PbO}, \text{AcO}_3$ . This tribasic acetate has long been known, in solution, under the name of *Goulard's Extract of Lead*. It is the *Liquor plumbi subacetatis* of the Pharmacopœia. It is prepared by boiling excess of finely-powdered protoxide of lead in a solution of the acetate, or in dilute acetic acid. About 15 parts of litharge to 10 of the crystallized acetate may be used; about 6 parts are dissolved; and the solution, filtered, and evaporated, leaves an anhydrous *trisacetate*. According to Payen, a tribasic acetate of lead is also thrown down, when slight excess of ammonia is added, drop by drop, to a cold solution of acetate of lead. At the temperature of  $212^\circ$ , 100 parts of water dissolve 18 parts of this salt, and the saturated solution yields silky crystals on cooling; it is insoluble in absolute alcohol. It has an alkaline reaction both on turmeric and litmus paper. It is a very susceptible test of the presence of carbonic acid, which it absorbs from the atmosphere, and suffers a proportionate decomposition: even distilled water is seldom so free from carbonic acid as not to be rendered turbid on the addition of a few drops of the solution of this salt. With all common spring and river water it forms a more or less turbid white mixture, known as *Goulard's lotion*. It forms precipitates in all solutions which affect the neutral acetate, and it throws down the greater number of organic compounds, hence its use in many cases of analysis. The anhydrous salt consists of

|                           |   |      |     |      |        |            |
|---------------------------|---|------|-----|------|--------|------------|
|                           |   |      |     |      |        | Berzelius. |
| Oxide of lead .....       | 3 | .... | 336 | .... | 86.82  | 86.77      |
| Acetic acid .....         | 1 | .... | 51  | .... | 13.18  | 13.23      |
| <hr/>                     |   |      |     |      |        | <hr/>      |
| Trisacetate of lead ..... | 1 |      | 387 |      | 100.00 | 100.00     |

*Hexacetate of Lead.*  $6\text{PbO}, \text{AcO}_3$ . When 1 part of acetate of lead and 3 of litharge are boiled together in water, or when a solution of the neutral acetate of lead is decomposed by considerable excess of ammonia, a white powder is obtained, of very sparing solubility even in hot water; but, as the boiling solution cools, plumose crystals separate, which, when carefully dried, consist of

|                             |   |      |     |      |        |            |
|-----------------------------|---|------|-----|------|--------|------------|
|                             |   |      |     |      |        | Berzelius. |
| Oxide of lead .....         | 6 | .... | 672 | .... | 89.60  | 91.3       |
| Acetic acid .....           | 1 | .... | 51  | .... | 6.80   | 5.7        |
| Water .....                 | 3 | .... | 27  | .... | 3.60   | 3.0        |
| <hr/>                       |   |      |     |      |        | <hr/>      |
| Hydrated hexacetate of lead | 1 |      | 750 |      | 100.00 | 100.0      |

*Acetate of Antimony.* This salt, formed by digesting protoxide of antimony in vinegar, was once employed as an emetic.

*Acetate of Bismuth* may be formed by adding nitrate of bismuth to a concentrated solution of acetate of potassa; a precipitate falls, which redissolves on the application of heat, and afterwards affords scaly crystals. The addition of acetic acid to nitrate of bismuth prevents its precipitation when diluted. (MORVEAU, *Ency. Méthod.*)



*Acetate of Uranium*,  $\text{UO}, \text{AcO}_3$ , crystallizes, according to Klaproth, in transparent yellow square prisms, soluble in water. Several of the *double acetates of uranium* have been described by Wertheim (*Poggend. Ann.*, 1842, and *Ann. Ch. et Ph.*, 3ème Sér., xi. 49.) When crystallized nitrate of uranium is so far decomposed by heat as to form a small portion of suboxide, the residue, dissolved in acetic acid and filtered, yields a solution which dissolves other bases; and when these are added till they begin to throw down oxide of uranium, and then a little acetic acid added so as to redissolve the precipitate, hot concentrated solutions may be obtained, of double salts composed of acetate of uranium in combination with the other acetate; he thus obtained the following compounds:

|                                 |  |
|---------------------------------|--|
| Uranio-acetate of potassa ..... | $\text{KO}, \text{AcO}_3 + 2[\text{U}_2 \text{O}_3, \text{AcO}_3] + 2\text{HO}$            |
| ” ” soda .....                  | $\text{NaO}, \text{AcO}_3 + 2[\text{U}_2 \text{O}_3, \text{AcO}_3]$                        |
| ” ” ammonia ....                | $\text{NH}_4 \text{O}, \text{AcO}_3 + 2[\text{U}_2 \text{O}_3, \text{AcO}_3] + 6\text{HO}$ |
| ” ” baryta .....                | $\text{BaO}, \text{AcO}_3 + 2[\text{U}_2 \text{O}_3, \text{AcO}_3] + 2\text{HO}$           |
| ” ” magnesia ....               | $\text{MgO}, \text{AcO}_3 + 2[\text{U}_2 \text{O}_3, \text{AcO}_3] + 8\text{HO}$           |
| ” ” zinc .....                  | $\text{ZnO}, \text{AcO}_3 + 2[\text{U}_2 \text{O}_3, \text{AcO}_3] + 3\text{HO}$           |
| ” ” silver .....                | $\text{AgO}, \text{AcO}_3 + 2[\text{U}_2 \text{O}_3, \text{AcO}_3] + 2\text{HO}$           |

*Acetate of Cerium*. Recently-precipitated oxide of cerium readily dissolves in acetic acid, and yields small crystals on evaporation, of a sweetish taste, permanent, and readily soluble in water. (HISINGER and BERZELIUS; *Gehlen's Jour.*, ii. 414.)

*Acetate of Chromium*. The acetate of the *protoxide* of chromium (PELIGOT, *Ann. Ch. et Ph.*, December, 1844,) is represented by the formula  $\text{C}_4 \text{H}_3 \text{O}_3, \text{CrO}, \text{HO}$ .

*Acetate of Suboxide of Mercury*,  $\text{Hg}_2 \text{O}, \text{AcO}_3$ , is most readily formed by mixing a solution of nitrate of suboxide of mercury with acetate of potassa. For this purpose, dissolve 3 ounces of mercury in about  $4\frac{1}{2}$  ounces of cold nitric acid, and mix this solution with 3 ounces of acetate of potassa previously dissolved in 8 pints of boiling water, and set the whole aside to crystallize, which takes place as the liquor cools, and the acetate of suboxide of mercury then separates in the form of micaceous crystalline plates, which are to be washed in cold water, and dried on blotting-paper. (*Edin. Pharm.*) In preparing this salt, the quantity of water for dissolving the acetate need not be so large as above directed, 1 pint being sufficient; but it is necessary to pour the mercurial solution into the acetate. This salt has an acrid taste, and is very difficultly soluble, requiring, according to Braconnot (*Ann. de Ch.*, LXXXvi. 92), 600 parts of water for its solution. It is insoluble in alcohol. It should be dried in the dark, as light has a tendency to decompose it. It was once used in medicine, especially as an ingredient in *Keyser's Pills*. It consists of

|                               |   |     |     |     |       | Dumas. | Garot. |
|-------------------------------|---|-----|-----|-----|-------|--------|--------|
| Dioxide of mercury .....      | 1 | ... | 208 | ... | 80.3  | ...    | 79.7   |
| Acetic acid .....             | 1 | ... | 51  | ... | 19.7  | ...    | 20.3   |
| Acetate of dioxide of mercury | 1 |     | 259 |     | 100.0 |        | 100.0  |

*Acetate of Mercury*,  $\text{HgO}, \text{AcO}_3$ , is obtained by boiling red oxide of mercury in dilute acetic acid; on cooling, nacreous crystals are deposited,

readily soluble in water. Alcohol and ether abstract the acid of this salt, and heat also expels it. This salt consists of

|                          |   |      |     |      |       | Stromeyer.  | Garot.   |
|--------------------------|---|------|-----|------|-------|-------------|----------|
| Red oxide of mercury.... | 1 | .... | 108 | .... | 67.9  | .... 67.664 | .... 67. |
| Acetic acid .....        | 1 | .... | 51  | .... | 32.1  | .... 32.336 | .... 33. |
| <hr/>                    |   |      |     |      |       |             |          |
| Peracetate of mercury    | 1 |      | 159 |      | 100.0 | 100.000     | 100.     |

*Acetate of Silver.*  $\text{AgO}$ ,  $\text{AcO}_3$ . This is a very difficultly soluble salt, and much resembles the acetate of suboxide of mercury. It is deposited in lamellar crystals when acetic acid is added to a strong solution of nitrate of silver; it is also abundantly precipitated from a mixed solution of nitrate of silver and acetate of soda. Its difficult solubility renders nitrate of silver useful occasionally as a test of acetic acid. It consists of

|                        |   |      |     |      |        | Dumas.     | Liebig and Redtenbacher. |
|------------------------|---|------|-----|------|--------|------------|--------------------------|
| Oxide of silver .....  | 1 | .... | 116 | .... | 69.46  | .... 70.33 | .... 69.399              |
| Acetic acid .....      | 1 | .... | 51  | .... | 30.54  | .... 29.67 | .... 30.601              |
| <hr/>                  |   |      |     |      |        |            |                          |
| Acetate of silver .... | 1 |      | 167 |      | 100.00 | 100.00     | 100.000                  |

*Acetate of Alumina.*  $\text{Al}_2\text{O}_3$ ,  $3\text{AcO}_3$ . This salt is extensively employed by dyers and calico-printers as a basis or mordant for fixing a great variety of colors: it is usually made by mixing solutions of alum and acetate of lead, or acetate of baryta. About 3 lbs. of alum are generally dissolved in 8 gallons of water, and a pound and a half of sugar of lead stirred into it; a copious formation of sulphate of lead ensues, which is allowed to subside, and the clear liquor, holding acetate of alumina, and a portion of undecomposed alum in solution, is then drawn off; a portion of pearlash or chalk being added to it previous to use, in order to saturate any excess of acid. This salt is also produced by the mutual decomposition of acetate of lime and alum. A gallon of a solution of acetate of lime, of a specific gravity of about 1.050, equivalent to nearly half a pound avoirdupois of dry acetic acid, is employed for every  $2\frac{3}{4}$  lbs. of alum. (URE'S *Dictionary*, Art. ALUMINA.)

Acetate of alumina is obtained by evaporation in the form of a gum-like mass, very soluble and deliquescent, and which loses acetic acid when only gently heated. When formed by digesting recently-precipitated alumina in acetic acid, it may be procured in deliquescent acicular crystals of an astringent taste, and containing, according to Richter, 73.81 acid + 26.19 alumina: hence it is probably a *binacetate*.

The solution of acetate of alumina, as usually prepared, becomes turbid when heated, and again transparent on cooling; a curious circumstance, first observed by Gay-Lussac, and depending upon a temporary decomposition of the salt; whether the deposit be alumina, or a subacetate, seems not understood; its formation is prevented in the solutions used by the calico-printer, by the presence of excess of alum.

ACETONE. PYROACETIC SPIRIT. PYROACETIC ETHER.  $\text{C}_3\text{H}_3\text{O}$ . This product was first obtained by Derosne, along with acetic acid, by the destructive distillation of acetate of copper. (*Ann. de Chim.*, lxxiii. 267.) Chenevix obtained it from other acetates. It has subsequently been



examined by Macaire and Marcet (*Ann. of Phil.*, N. S., viii. 69,) by Liebig and Dumas, (*Ann. Ch. et Ph.*, xlix,) and others. When dry acetate of lime is carefully distilled, it yields a considerable portion of this product; it may be freed from water and empyreumatic oil, by repeated rectification over chloride of calcium. Acetone is also formed during the dry distillation of anhydrous acetate of lead. (WÖHLER.) Zeise gives the following as the best process for the preparation of acetone. 1 part of dry quicklime and 2 parts of crystalline sugar of lead are well pulverized and mixed, and introduced into a retort, or iron bottle; after a time the lime becomes hydrated at the expense of the water of crystallization of the acetate, and much heat is evolved. The retort is then adapted to a receiver immersed in a freezing mixture, or in ice, and heat gradually applied to it till red hot. The crude product is a mixture of acetone, water, and two oily bodies; it is redistilled in a water-bath off chloride of calcium, and the distillate is then again poured upon chloride of calcium, and after some days is poured off, and three-fourths of it distilled over.

Acetone, when pure, is a colorless limpid liquid, highly inflammable, of a peculiar penetrating and somewhat aromatic odor; specific gravity = 0.792 at 64°. It boils at 132°, and the density of its vapor is, according to Dumas, 2.019. It mixes in all proportions with water, alcohol, ether, and oil of turpentine; it is not affected by exposure to air; it may be distilled without change over the caustic alkalis; but when mixed with fixed alkaline solutions, and exposed to air, oxygen is absorbed, and a brown matter slowly formed. It dissolves saline substances generally less copiously than alcohol. Distilled with chloride of lime it yields *chloroform*. Gaseous chlorine is absorbed by it, with the evolution of hydrochloric acid, and the formation of a peculiar oily fluid, of the specific gravity 1.33, and composed of  $C_3H_2OCl$ . (LIEBIG.) The action of acetone on deutochloride of platinum has been studied by Zeise, (*Ann. Ch. et Ph.*, lxxii. 113,) as also the mutual action of acetone and phosphorus. (*Ibid.*, 1842, vi. 501.)

The ultimate components of acetone are

|               |   |      |    |      |       | Dumas. | Macaire<br>and Marcet. |      | Liebig. |      |        |
|---------------|---|------|----|------|-------|--------|------------------------|------|---------|------|--------|
| Carbon .....  | 3 | .... | 18 | .... | 62·1  | ....   | 62·5                   | .... | 55·30   | .... | 62·49  |
| Hydrogen .... | 3 | .... | 3  | .... | 10·3  | ....   | 10·2                   | .... | 8·20    | .... | 10·47  |
| Oxygen .....  | 1 | .... | 8  | .... | 27·6  | ....   | 27·3                   | .... | 36·50   | .... | 27·04  |
| <hr/>         |   |      |    |      |       |        |                        |      |         |      |        |
| Acetone ....  | 1 |      | 29 |      | 100·0 |        | 100·0                  |      | 100·00  |      | 100·00 |

The product analyzed by Macaire and Marcet was probably not pure. Liebig and Dumas have observed that *anhydrous acetate of baryta* is resolved by heat into acetone and carbonate of baryta, and it will be found that 1 equivalent of acetic acid,  $C_4H_3O_3$ , may be exactly resolved into 1 equivalent of acetone,  $C_3H_3O$ , and 1 of carbonic acid,  $CO_2$ .

**METACETONE. OXIDE OF METACETYLE.  $C_6H_5O$ .** Fremy has given this name to a product obtained by distilling a mixture of 1 part of starch, or of sugar, with 8 of quicklime, in a sufficiently capacious retort. The water which the lime abstracts from the starch soon causes so high a temperature, as to enable the process to go on without further heat. The crude oil-like product which passes over, requires to be shaken with

water, which abstracts acetone, and the remaining impure *metacelone* is purified by re-distillation, the first portion which goes over being rejected, and the latter portion collected, and dehydrated by distillation off chloride of calcium.

*Metacetone* is a colorless liquid, insoluble in water, but soluble in alcohol and ether; it has an agreeable odor: it boils at  $183^{\circ}$ , and the density of its vapor is 3.25. (*Ann. Ch. et Ph.*, Lix. 5.) It consists of

|                 |   |       |    |       |        |       |        |
|-----------------|---|-------|----|-------|--------|-------|--------|
| Carbon .....    | 6 | ..... | 36 | ..... | 73.47  | ..... | Fremy. |
| Hydrogen .....  | 5 | ..... | 5  | ..... | 10.20  | ..... | 72.37  |
| Oxygen .....    | 1 | ..... | 8  | ..... | 16.33  | ..... | 10.15  |
| <hr/>           |   |       |    |       |        |       | 17.48  |
| Metacetone .... | 1 |       | 49 |       | 100.00 |       | 100.00 |

**METACETONIC ACID. METACETYLIC ACID.**  $C_6 H_5 O_3, + HIO$ . This acid, discovered by Gottlieb, is formed during the distillation of a mixture of metacetone with sulphuric acid and bichromate of potassa. It may also be obtained as the result of the action of hydrate of potassa upon sugar; for this purpose Gottlieb prepares a hot solution of caustic potassa, so strong as to concrete on cooling, to which he adds a quantity of sugar equal to one-third of the weight of the potassa dissolved; the mixture becomes brown, and evolves hydrogen, and carbonic, oxalic, formic, acetic, and metacetonic acids are at the same time formed, which remain combined with the potassa. When this product has cooled, it is introduced into a capacious retort, and distilled with excess of sulphuric acid. The distillate is then boiled with oxide of mercury to decompose the formic acid, and the mercury is separated from the liquor by sulphuretted hydrogen. The remaining solution, which now contains acetic and metacetonic acid, is saturated by carbonate of soda; the resulting acetate of soda is as far as possible removed by repeated crystallizations, so as to leave the more soluble *metacetone of soda*, which is finally decomposed by sulphuric acid and distillation. The *metacetonic acid* which passes over, has a peculiar empyreumatic greasy odor. It consists of

|                               |     |     |    |     |        |       |           |   |     |    |     |        |
|-------------------------------|-----|-----|----|-----|--------|-------|-----------|---|-----|----|-----|--------|
| Carbon .....                  | 6   | ... | 36 | ... | 48·65  | } = { | Anhydrous | 1 | ... | 65 | ... | 87·84  |
| Hydrogen.....                 | 6   | ... | 6  | ... | 8·10   |       | acid..... |   |     |    |     |        |
| Oxygen .....                  | 4   | ... | 32 | ... | 43·25  |       | Water ... | 1 | ... | 9  | ... | 12·16  |
| <hr/>                         |     |     |    |     |        |       |           |   |     |    |     |        |
| Hydrated metacetic acid ..... | } 1 |     | 74 |     | 100·00 |       |           | 1 |     | 74 |     | 100·00 |

**CHLORACETIC ACID.**  $C_4 Cl_3 O_3 + HO$ . This compound was discovered by Dumas (*Sur les Types Chimiques*, *Ann. Ch. et Ph.*, LXXiii. 77.) It is formed by introducing a small quantity of concentrated acetic acid into bottles filled with dry chlorine and exposed to the direct sunshine; white vapors are soon formed, and a liquid, drops of which condense in the upper part of the bottles, and the chlorine gradually disappears. On hot days, and in bright sunshine, the action is sometimes so intense as to occasion explosion; this, however, rarely happens; and never immediately on exposure. The next day a dense liquid is found at the bottom of the bottles, and their interiors are lined with a crystalline deposit, chiefly



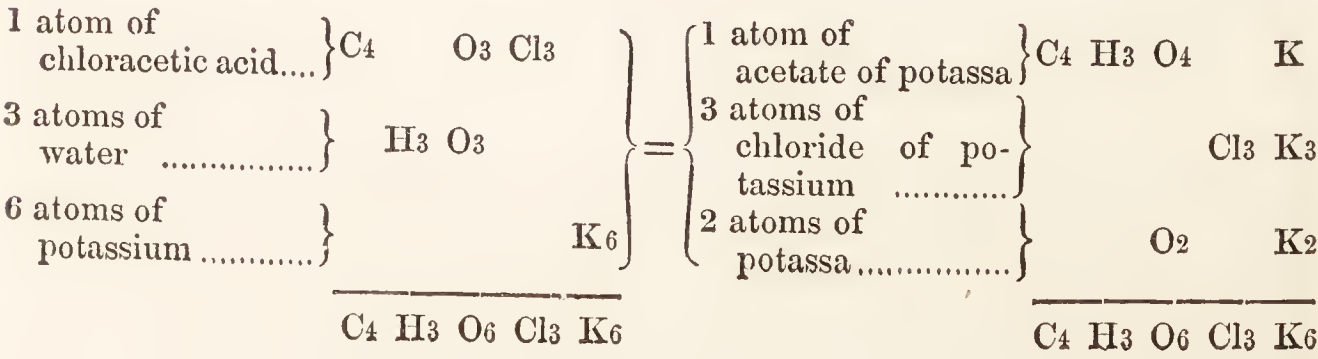
consisting of chloracetic acid, with a little oxalic acid. When the bottles are first opened, a gas which had been compressed within them escapes, composed of hydrochloric acid with some carbonic acid, and a suffocating vapor having the odor of chlorocarbonic acid. If the bottles be left for some hours, the crystals gradually deliquesce into a concentrated solution of chloracetic acid, leaving a small quantity of crystals of oxalic acid; but it is better to wash the bottles with a small quantity of water, which, poured into them successively, yields a strong chloracetic solution, and which, exposed *in vacuo* by the side of a vessel containing pieces of caustic potassa, and another containing sulphuric acid, may be dehydrated; the oxalic acid first crystallizes, and then the chloracetic acid; the latter forms well-defined rhombohedric crystals. If the liquor refuses to crystallize, it may be distilled with some anhydrous phosphoric acid, which abstracts the water and decomposes the oxalic acid, without exerting any action upon the chloracetic acid; as the acetic acid is more volatile than the chloracetic, the last portions of the distillate should be collected apart, and when set aside, deposit crystals of the chloracetic acid.

The first crop of crystals contain interposed acetic acid, which may be removed by wrapping them in bibulous paper and exposing them for 24 hours in a vacuum; the whole of the acetic acid is thus transferred to the paper.

*Chloracetic acid* is colorless, has a slight odor, and a pungent caustic taste; it bleaches the tongue, like oxygenated water, and blisters and disorganizes the cuticle. It is deliquescent, and very soluble in water. Its vapor is dangerously irritating. It is very acid, but has no bleaching power upon vegetable colors. It fuses at 115°, and at that temperature its sp. gr. is 1·6. It boils at between 385° and 390°; the density of its vapor, (4 volumes of which represent 1 atom of the acid) is 5·6. In this acid the whole of the hydrogen of the anhydrous acetic acid is replaced by chlorine; the crystals contain 1 atom of water; their ultimate components are,

|  |                      |         |           |      |                |  |   |       |         |
|--|----------------------|---------|-----------|------|----------------|--|---|-------|---------|
| Dumas.                                 |                      |         |           |      |                |  |   |       |         |
| Carbon .....                           | 4....                | 24....  | 14·95.... | 15·6 | } = {          | Anhydrous<br>chloracetic<br>acid ..... | } | 1.... | 156.... |
| Hydrogen .....                         | 1....                | 1....   | 0·61....  | 0·7  |                |  |   |       |         |
| Oxygen .....                           | 4....                | 32....  | 19·56.... | 19·9 |                |  |   |       |         |
| Chlorine.....                          | 3....                | 108.... | 64·88.... | 63·8 |                |  |   |       |         |
| <hr/>                                  |                      |         |           |      |                |  |   |       |         |
| Crystallized chloracetic<br>acid ..... | } 1 165 100·00 100·0 |         |           |      | } 1 165 100·00 |  |   |       |         |

When a concentrated aqueous solution of chloracetic acid is acted upon by amalgam of potassium, (150 of mercury to 1 potassium) acetate of potassa, chloride of potassium, and potassa are the results. (MELSENS. KOLBE. *Ann. der Pharm.*, xlix. 340.)



When chloracetic acid is boiled with excess of ammonia, chloroform and carbonate of ammonia are produced.  $\text{C}_4\text{Cl}_3\text{O}_3 + \text{HO} = \text{C}_2\text{HCl}_3 + 2[\text{CO}_2]$ .

When a solution of potassa is used instead of ammonia, a period occurs at which the fluid continues to boil spontaneously till the action ceases; chloroform and carbonate of potassa are formed, but a part of the chloroform is also at the same time decomposed, producing formiate of potassa and chloride of potassium.

*Chloracetate of Ammonia.*  $\text{NH}_4\text{O}, \text{C}_4\text{Cl}_3\text{O}_3, + 4\text{HO}$ . Dumas obtained crystals of this salt by evaporating a solution of the acid neutralised by ammonia, *in vacuo*. Dried *in vacuo* over sulphuric acid, it became anhydrous.

*Chloracetate of Potassa,*  $\text{KO}, \text{C}_4\text{Cl}_3\text{O}_3, + 2\text{HO}$ , was obtained by neutralising the acid with carbonate of potassa, and spontaneous evaporation; it formed silky crystals, slightly deliquescent in very moist air, and decomposed with a kind of explosion when heated. When a solution of this salt is boiled with excess of potassa, the liquor deposits, on cooling, an abundant crop of crystals of chloride of potassium, and the mother-liquor acts powerfully upon a solution of nitrate of silver, after the manner of the formiates.

*Chloracetate of Silver.*  $\text{AgO}, \text{C}_4\text{Cl}_3\text{O}_3$ . When moist oxide of silver is dissolved in a strong solution of chloracetic acid, grey lamellar crystals are formed; on the addition of water these dissolve, and on evaporation *in vacuo*, granular crystals of the salt are obtained. Heated upon a piece of paper this salt suddenly fuses, evolves vapor of a chloracetic odor, and leaves chloride of silver. The components of this salt are

|                             |   |       |     |       |        | Dumas.        |
|-----------------------------|---|-------|-----|-------|--------|---------------|
| Carbon.....                 | 4 | ..... | 24  | ..... | 9.04   | ..... 8.91    |
| Chlorine .....              | 3 | ..... | 108 | ..... | 39.23  | } ..... 51.10 |
| Oxygen .....                | 3 | ..... | 24  | ..... | 11.82  |               |
| Oxide of silver .....       | 1 | ..... | 116 | ..... | 39.91  | ..... 39.89   |
| <hr/>                       |   |       |     |       |        |               |
| Chloracetate of silver..... | 1 |       | 272 |       | 100.00 | 100.00        |

*Chloracetate of Oxide of Ethyle.*  $\text{AeO}, \text{C}_4\text{Cl}_3\text{O}_3$ . Dumas prepared this compound by distilling chloracetic acid, or a chloracetate, with alcohol and sulphuric acid. Water added to the product separates the chloracetic ether in the form of a heavy colorless oil, having the odor of chloride of ethyle.

*Terchloride of Acetylene.*  $\text{C}_2\text{HCl}_3$ . This compound, in which the oxygen of acetic acid is replaced by chlorine, was obtained by Regnault, by the action of chlorine upon chloride of ethyle ( $\text{C}_2\text{H}_5\text{Cl}$ ) under the influence of the direct solar rays. The first compound which he obtained as the result of this action was  $= \text{C}_2\text{H}_4\text{Cl}_2$ , and from this, by the further action of chlorine and light, he succeeded in obtaining the above chloride of acetylene, in which the whole of the oxygen of the acetic acid is replaced by chlorine. (*Ann. Ch. et Ph.*, LXXI. 355.) It is a fluid of an ethereal odor and a sweet taste; it boils at  $167^\circ$ : the density of its vapor is 4.61; under the further influence of chlorine, it has its atoms of hydrogen successively replaced by those of chlorine, till at length a chloride of carbon  $= \text{C}_2\text{Cl}_6$  or  $2[\text{C}_2\text{Cl}_3]$  is the result.

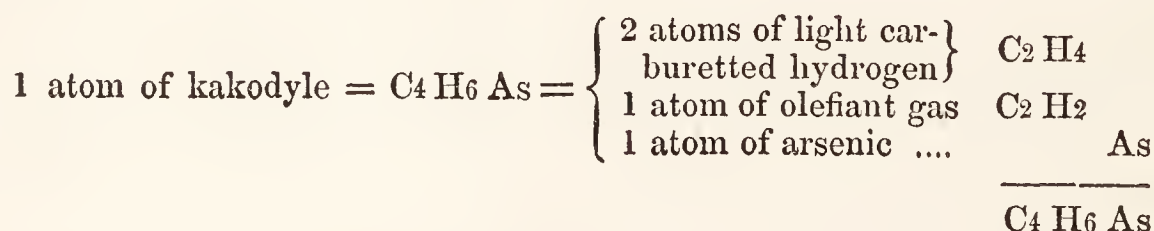


§ XVII. KAKODYLE.  $C_4 H_6 As = Kd.$ 

This arsenical radical, the name of which (from *κακος* *bad*, and *οδωδη* *odor*,) implies its offensive smell, exists as the *basis* of a compound long known under the name of *Cadet's fuming liquor*; it has been isolated, and many of its compounds examined by Bunsen. (*Ann. der Pharm.*, xxiv. 271; xxvii. 148; xxxi. 175; xxxvii. 1; xlii. 25; and xlv. 1.)

*Kakodyle* is obtained by the action of perfectly clean metallic zinc upon pure anhydrous *chloride of kakodyle*; the substances should be introduced into a glass flask, previously filled with carbonic acid, and then hermetically sealed, and exposed to a temperature of  $212^{\circ}$  in a water-bath. The metal dissolves, and on cooling, a white crystalline mass is formed, which on the addition of a little water dissolves, and deposits the kakodyle in the form of a heavy oil-like liquid; it requires to be purified, by distilling it off a fresh portion of zinc. The proper apparatus for these operations is described by Bunsen in the *Annalen* above quoted. (xlii. 25.)

Kakodyle is a clear and highly refractive liquid, which when cooled to  $20^{\circ}$ , crystallizes in transparent square prisms. Its specific gravity is 1.48, and the density of its vapor is 7.2. When dropped through the air, or into oxygen, or chlorine, it immediately takes fire; in oxygen it burns with a blue flame, forming water, and carbonic and arsenious acid; the latter rises as a white smoke. At a temperature a little below redness, it is resolved into metallic arsenic, light carburetted hydrogen, and olefiant gas, without any carbonaceous deposit.



The components of kakodyle are

|               |   |       |     |       |        | Bunsen.     |
|---------------|---|-------|-----|-------|--------|-------------|
| Carbon.....   | 4 | ..... | 24  | ..... | 22.86  | ..... 22.80 |
| Hydrogen .... | 6 | ..... | 6   | ..... | 5.71   | ..... 5.48  |
| Arsenic ..... | 1 | ..... | 75  | ..... | 71.43  | ..... 71.72 |
| <hr/>         |   |       |     |       |        |             |
| Kakodyle .... | 1 |       | 105 |       | 100.00 | 100.00      |

OXIDE OF KAKODYLE. ALKARSINE. CADET'S FUMING LIQUOR.  $C_4 H_6 As O, = KdO.$  Equal weights of arsenious acid and acetate of potassa are intimately mixed, and gradually raised to a red-heat in a glass retort, connected with a receiver surrounded by ice. This, and the subsequent operations, should be performed in the open air, in consequence of the poisonous character of the evolved vapors. Metallic arsenic is found in the receiver, together with two liquids, the heavier of which is *oxide of kakodyle*, and the lighter, a mixture of acetone, acetic acid, and water. The gases given off during the operation are chiefly carburetted hydrogen and carbonic acid, and the residue in the retort consists of car-

bonate of potassa and charcoal. The oxide of kakodyle is separated, and washed, in vessels filled with carbonic acid, with water deprived of air; it is finally purified by distilling it off caustic potassa in a vessel filled with hydrogen gas. (Bunsen has described the requisite apparatus for these distillations in *Poggendorf's Annalen*, XL. 223.)

*Oxide of kakodyle* is a colorless highly refractive liquid, which does not mix with water, but imparts to it a strong alliaceous odor. Its specific gravity is 1.64. It dissolves, in all proportions, in alcohol and in ether, and is separated from its solution in alcohol, by water. Its boiling-point is about  $300^{\circ}$ , and the density of its vapor = 7.8. It congeals into a white crystalline mass at  $9^{\circ}$ . Its odor is insupportably nauseous, and long adheres to the clothes. Its vapor is extremely irritating. It dissolves sulphur and phosphorus. When exposed to the air it emits dense white fumes, becomes hot, and ultimately bursts into flame, producing water and carbonic acid, and the white fumes of arsenious acid. Under the slow access of air, or at a very low temperature, it passes into arsenious and kakodylic acid, *parakakodylic oxide* being at the same time formed. It explodes and inflames on contact with nitric acid. In chlorine it takes fire and burns with a smoky flame, forming chloride of arsenic and hydrochloric acid. It is also inflamed by bromine. It dissolves iodine, and forms with it a white crystalline compound. Potassium retains its metallic lustre in it for some time; but if heated, an explosion ensues. Its components are

|                   |   |     |     |     |        |       |          |   |     |     |     |       |
|-------------------|---|-----|-----|-----|--------|-------|----------|---|-----|-----|-----|-------|
| Carbon .....      | 4 | ... | 24  | ... | 21.24  | } = { | Kakodyle | 1 | ... | 105 | ... | 92.9  |
| Hydrogen .....    | 6 | ... | 6   | ... | 5.30   |       |          |   |     |     |     |       |
| Arsenic .....     | 1 | ... | 75  | ... | 66.37  |       | Oxygen   | 1 | ... | 8   | ... | 7.1   |
| Oxygen .....      | 1 | ... | 8   | ... | 7.09   |       |          |   |     |     |     |       |
| <hr/>             |   |     |     |     |        |       |          |   |     |     |     |       |
| Oxide of kakodyle | 1 |     | 113 |     | 100.00 |       |          | 1 |     | 113 |     | 100.0 |

KAKODYLIC ACID. ALKARGEN.  $C_4H_6AsO_3 + HO, = KdO_3, HIO$ . This acid is, as above stated, produced by the action of air on oxide of kakodyle. It is best obtained by adding red oxide of mercury to oxide of kakodyle under water, which should be kept cold. As soon as the mixture has become inodorous, the liquid portion is poured off from the reduced mercury, and, in order to decompose any kakodylate of mercury which may have been formed, oxide of kakodyle may be added till its odor remains slightly perceptible. The solution is then evaporated, and the residue dissolved in alcohol, from which crystallized kakodylic acid may be obtained.

*Kakodylic acid* forms large transparent inodorous crystals in the form of four-sided prisms, of a slightly sour taste, and deliquescent in a damp atmosphere. They are abundantly soluble in water, less soluble in alcohol, and insoluble in ether. Heated to  $392^{\circ}$  this acid fuses, and at about  $446^{\circ}$  it is decomposed, forming arsenious acid, and fetid arseniferous products. It appears from Bunsen's experiments, that this acid is not poisonous; injected in the quantity of 6 or 7 grains into the stomach, and even into the blood of a rabbit, it produced no ill effect. Kakodylic acid forms amorphous gum-like combinations with the alkalis; but with oxide of mercury, and oxide of silver, it yields crystallizable salts. The components of the *crystallized* or *hydrated acid*, are



|                                   |   |     |     |     |        | Bunsen. |
|-----------------------------------|---|-----|-----|-----|--------|---------|
| Carbon .....                      | 4 | ... | 24  | ... | 17.63  | 17.44   |
| Hydrogen .....                    | 7 | ... | 7   | ... | 5.07   | 5.01    |
| Arsenic .....                     | 1 | ... | 75  | ... | 54.25  | 56.27   |
| Oxygen .....                      | 4 | ... | 32  | ... | 23.05  | 21.28   |
| <hr/>                             |   |     |     |     |        |         |
| Crystallized kakodylic acid ..... | 1 |     | 138 |     | 100.00 | 100.00  |

CHLORIDE OF KAKODYLE.  $\text{KdCl}$ . When a dilute alcoholic solution of oxide of kakodyle is mixed with a similar solution of corrosive sublimate, a white crystalline precipitate falls, which is  $\text{KdO}, 2\text{HgCl}$ , and which, when distilled with hydrochloric acid, yields *chloride of kakodyle*. This compound, when dehydrated by distillation off chloride of calcium, forms a clear colorless liquid, very inflammable, of a most offensive and irritating odor, and eminently poisonous. It sinks in, and is insoluble in water and in ether; but soluble in alcohol. Its boiling-point is a little above  $212^\circ$ , and the density of its vapor is 4.56. It forms a *hydrate*, which is thick and viscid, and easily decomposed by distillation off chloride of calcium. Concentrated nitric acid decomposes it with explosion. It combines with subchloride of copper, forming a white insoluble crystalline double salt,  $= \text{KdCl} + \text{Cu}_2\text{Cl}$ .

In the preparation of this, and other kakodylic compounds, a red pulverulent substance often makes its appearance, which has been termed *Erythrarsine*, and which is  $= \text{C}_4\text{H}_6\text{As}_3\text{O}_3$ . It is insoluble in water, and in alcohol and ether, and when long exposed to air yields arsenious acid.

IODIDE OF KAKODYLE,  $\text{KdI}$ , is obtained by distilling a mixture of oxide of kakodyle and strong aqueous solution of hydriodic acid. It is a yellowish liquid, having the nauseating and poisonous odor of the chloride. It boils at a little above  $212^\circ$ , yielding a yellow vapor, the density of which is 7.9. It is insoluble in water, but soluble in ether and alcohol.

BROMIDE OF KAKODYLE,  $\text{KdBr}$ , is a yellow liquid, closely resembling the chloride. With water it yields hydrobromic acid, and *oxibromide* of kakodyle.

FLUORIDE OF KAKODYLE,  $\text{KdF}$ , has an insupportably nauseous odor, and in other respects resembles the chloride.

SULPHURET OF KAKODYLE.  $\text{KdS}$ . This compound is obtained by distilling a mixture of kakodyle with hydrosulphuret of sulphuret of barium; it is a clear, thin, colorless liquid, of a nauseous and very adherent odor; it boils at somewhat above  $212^\circ$ , but its vapor, the density of which is 7.7, readily passes over with that of water. It is insoluble in water, but soluble in alcohol and ether. It dissolves sulphur, forming a persulphuret,  $= \text{KdS}_3$ , which acts as a *sulphur-acid*, and forms salts with the sulphurets of copper, lead, bismuth, antimony, and gold.

SELENIURET OF KAKODYLE,  $\text{KdSe}$ , closely resembles the sulphuret.

CYANIDE OF KAKODYLE, Kd Cy. This compound is formed by distilling a concentrated solution of cyanide of mercury with oxide of kakodyle. Metallic mercury is separated, and some kakodylic acid formed, and on applying heat, the *cyanide* distils over. At about  $90^{\circ}$  it is a colorless liquid, but at lower temperatures it forms very brilliant prismatic crystals. It boils at about  $284^{\circ}$ . It is slightly soluble in water, and not very inflammable. It has a most offensive odor, and is eminently poisonous. When the air of a room is contaminated by the evaporation of a few grains of this cyanide, it causes vomiting, numbness of the extremities, fainting, and other highly alarming symptoms; so that the utmost caution is required in its examination.

The preceding are only a few of the combinations of kakodyle which have been examined with laborious minuteness by Bunsen: for the details I must refer to his papers above quoted. An excellent account of them will also be found in Löwig's work on *Organic Chemistry*, ii. 445.

§ XVIII. PYROXYLIC ALCOHOL. WOOD SPIRIT.  $C_2 H_4 O_2$   
 $= C_2 H_3 O, HO$ ; or,  $MeO, HO$ .

This compound, which, in reference to its correspondence with the *ethylic* series, has been termed *hydrate of oxide of methyle*, (from  $\mu\epsilon\theta\nu$  wine, and  $\iota\lambda\eta$  wood), was discovered by P. Taylor (*Quart. Jour. of Science*, xiv. 436); it was afterwards examined by Macaire and Marcet (*Bibl. Univ. and Ann. of Phil.*, N.S., viii. 62), then by Döberiner, by Colin, and by Liebig, by Dumas and Peligot, (DUMAS, *Chim. app. aux Arts*, v. 419, and *Ann. Ch. et Ph.*, lviii. 5), and by Kane (*Ann. der Pharm.*, xix. 164.)

When wood is subjected to destructive distillation there is formed, along with the tar, acetic acid, and other products already described, (p. 1210), a variable portion, but not amounting on an average to more than about 1 *per cent.* of an inflammable and volatile liquid; it may be separated, to a certain extent, from the water and acetic acid, by distillation and separation of the first products; and these, redistilled and rectified over quicklime, afford the *pyroxylic spirit*, or *alcohol of wood*, of commerce. If it contain ammonia, it must be neutralized, previous to its last rectification, by sulphuric acid.

To obtain perfectly pure pyroxylic spirit, Kane adds to it excess of chloride of calcium, and distils the mixture in a water-bath as long as volatile matter (consisting of acetone and other products) goes over; a compound of the pyroxylic spirit with chloride of calcium remains in the retort, to which he adds a quantity of water equal to that of the original spirit, and then continues the distillation. The product which is now obtained, and which is pure pyroxylic spirit diluted by a little water, may be dehydrated by a final distillation off quicklime.

*Pyroxylic spirit*, *wood-spirit*, or *hydrate of oxide of methyle*, (for it is the *alcohol* of the *methylic* series,) is a limpid liquid, of a peculiar odor, partaking of that of alcohol and acetic ether, with an aromatic taint which has been compared to peppermint. Its taste is hot and pungent. Its specific gravity at  $60^{\circ}$  is about 0.800. It is very inflammable,



and burns with a pale flame resembling that of alcohol. It boils at  $150^{\circ}$  ( $151.7$  under a pressure of  $29.96$  in mercury); if heated in a retort, even in a water-bath, the sudden extrications of its vapor are troublesome, and may be prevented by the presence of a little mercury, which equalizes the distribution of heat. The density of its vapor is  $1.125$  ( $1.120$  at  $212^{\circ}$ ). When pure it is not altered by exposure to air or light, but when subjected to the slow action of black platinum it yields, together with other products, *formic* acid; not acetic acid, as is the case with alcohol. It mixes in all proportions with water, alcohol, and ether, without becoming turbid; it does not form a black precipitate with proto-nitrate of mercury, and has no action on vegetable test papers.

Chlorine acts less powerfully on pyroxylic spirit than on alcohol, and according to Dumas and Peligot, heat is required to accelerate their mutual action; it then gives rise to the production of two liquids of very different degrees of volatility; that which is least volatile forms a crystallizable compound with ammonia. According to Kane, the action of chlorine on this spirit, under the influence of light, is violent and even attended by inflammation; in the absence of light, the gas is quietly absorbed under the abundant production of hydrochloric acid, and a thick liquid is formed, composed of  $C_6H_2O_2Cl_3$ . Chloride of lime acts upon pyroxylic spirit as it does upon alcohol, and chloroform is one of the products: it also dissolves potassa and soda with similar phenomena. It dissolves baryta with the evolution of heat; and with solution of potassa and sulphuret of carbon, it forms a product which resembles Zeise's hydroxanthate of potassa. Its solvent powers, in regard to *salts*, closely resemble those of alcohol, and it has been stated that it may be substituted for alcohol in the preparation of fulminating silver, though the action is less violent, and the product smaller in quantity; but, according to Dumas and Peligot, the product is *oxalate*, and not fulminate of silver; so also it converts nitrate into oxalate of mercury. Sulphur and phosphorus are to a certain extent soluble in it. It dissolves the resins, and may be used as an excellent substitute for alcohol in almost all varnishes; indeed, its superior volatility renders it preferable. It is a powerful antiseptic, and has been found a most effectual preservative of subjects for dissection.

Pyroxylic spirit has been analysed by several chemists: its components are

|                       |   |     |    |     | Dumas and<br>Peligot. |     |       |       |         |   |     |    |     |        |
|-----------------------|---|-----|----|-----|-----------------------|-----|-------|-------|---------|---|-----|----|-----|--------|
| Carbon .....          | 2 | ... | 12 | ... | 37.50                 | ... | 37.7  | } = { | Methyle | 1 | ... | 15 | ... | 46.89  |
| Hydrogen.....         | 4 | ... | 4  | ... | 12.50                 | ... | 12.5  |       | Oxygen  | 1 | ... | 8  | ... | 25.00  |
| Oxygen .....          | 2 | ... | 16 | ... | 50.00                 | ... | 49.8  |       | Water   | 1 | ... | 9  | ... | 28.11  |
| <hr/>                 |   |     |    |     |                       |     |       |       |         |   |     |    |     |        |
| Pyroxylic alcohol.... | 1 |     | 32 |     | 100.00                |     | 100.0 |       |         | 1 |     | 32 |     | 100.00 |

When pure *baryta* is digested in wood-spirit, heat is evolved, and on evaporating the resulting solution in vacuo, acicular crystals of a silky lustre are obtained =  $BaO + C_2H_4O_2$ . (DUMAS.) The compound above alluded to of *chloride of calcium and wood-spirit*, is obtained when the chloride is dissolved in purified wood-spirit; heat is evolved, and on cooling, the liquor deposits hexangular crystals, which deliquesce in a humid atmosphere, and consist of  $CaCl + 2[C_2H_4O_2]$ . (KANE.)

OXIDE OF METHYLE. METHYLIC ETHER.  $C_2H_3O = MeO$ . When 1 part of pyroligneous spirit is distilled with 4 of sulphuric acid, (Liebig uses equal volumes of spirit and acid,) abundance of gas is evolved; when collected over mercury it is found to consist of oxide of methyle, mixed with carbonic acid and sulphurous acid; the latter gases may be abstracted by potassa, or by milk of lime. Or the crude gas may be in the first instance passed through milk of lime, and then through bottles containing pure water, which absorbs the oxide of methyle; on boiling this solution the oxide is evolved, and may be collected over mercury.

Oxide of methyle is a colorless gas of an ethereal odor: its sp. gr. is 1.59; it burns with a pale blue flame; it is not liquefied at  $0^\circ$ . Water dissolves about 37 volumes of this gas, and acquires an ethereal and pungent smell and taste. It is taken up more abundantly by alcohol and by ether. It is also absorbed by oil of vitriol, and on adding water to this sulphuric solution, the methylic ether escapes with effervescence. Its components are, according to Dumas and Peligot,

|                  |   |     |    |     |        |       |         |   |     |    |     |        |
|------------------|---|-----|----|-----|--------|-------|---------|---|-----|----|-----|--------|
| Carbon .....     | 2 | ... | 12 | ... | 52.17  | } = { | Methyle | 1 | ... | 15 | ... | 65.22  |
| Hydrogen .....   | 3 | ... | 3  | ... | 13.04  |       |         |   |     |    |     |        |
| Oxygen .....     | 1 | ... | 8  | ... | 34.79  |       | Oxygen  | 1 | ... | 8  | ... | 34.78  |
| <hr/>            |   |     |    |     |        |       |         |   |     |    |     |        |
| Oxide of methyle | 1 |     | 23 |     | 100.00 |       |         | 1 |     | 23 |     | 100.00 |

This gas, therefore, is isomeric with alcohol, and the difference in their respective properties depends upon the different densities of their hydrocarbon; the hydrogen and carbon which constitute 1 atom of alcoholic hydrocarbon, forming 2 atoms of methylic hydrocarbon.

CHLORIDE OF METHYLE.  $C_2H_3Cl = MeCl$ . This compound is best obtained by heating a mixture of 2 parts of chloride of sodium, 1 of pyroxylic spirit, and 3 of sulphuric acid; a gas is evolved, which may be received over water, and which is pure chloride of methyle, any impurities being abstracted by the water. This gas is not condensable at  $0^\circ$ ; it is colorless, of an ethereal odor, and sweet taste, and burns with a greenish white flame. Water at  $60^\circ$  dissolves 2.5 volumes. It is quite neutral, and gives no precipitate with solution of nitrate of silver, resembling in these respects chloride of ethyle. Its density, determined by experiment, is 1.736.

When chloride of methyle is passed through a red-hot tube, it is resolved into hydrochloric acid, and a gaseous hydrocarbon which burns with a yellow flame, and is condensed by chlorine under exposure to light. Heated with caustic potassa chloride of methyle evolves hydrogen and formiate of potassa is formed, which by farther decomposition yields carbonate of potassa. In ordinary daylight chlorine produces no change on chloride of methyle; but in the direct rays of the sun the following compounds are successively formed, namely,  $C_2H_2Cl_2$ ;  $C_2HCl_3$ ; and  $C_2Cl_4$ .

The components of chloride of methyle are

|                     |   |      |    |      |        |     |          |   |      |    |      |        |  |
|---------------------|---|------|----|------|--------|-----|----------|---|------|----|------|--------|--|
| Carbon.....         | 2 | .... | 12 | .... | 23.53  | } = | Methyle  | 1 | .... | 15 | .... | 29.41  |  |
| Hydrogen '.....     | 3 | .... | 3  | .... | 5.88   |     |          |   |      |    |      |        |  |
| Chlorine .....      | 1 | .... | 36 | .... | 70.59  |     | Chlorine | 1 | .... | 36 | .... | 70.59  |  |
| <hr/>               |   |      |    |      |        |     |          |   |      |    |      |        |  |
| Chloride of methyle | 1 |      | 51 |      | 100.00 |     |          | 1 |      | 51 |      | 100.00 |  |



IODIDE OF METHYLE,  $C_2 H_3 I = Me I$ , is formed by distilling a mixture of 1 part of phosphorus, 8 of iodine, and 15 of wood-spirit: when the first action has ceased, the mixture is slowly raised to its boiling point, and the distillation continued as long as ethereal liquid goes over. This distillate consists of the iodide of methyle and undecomposed wood-spirit; the latter is abstracted by water, and the iodide rectified over chloride of calcium and oxide of lead. Its sp. gr. is 2.23. It is colorless, insoluble in water, difficultly combustible, and boils at about  $110^\circ$ , yielding vapor of the density = 4.88.

It consists of

|                   |   |     |     |     | Dumas and<br>Peligot. |     |        |             |            |     |     |     |        |       |
|-------------------|---|-----|-----|-----|-----------------------|-----|--------|-------------|------------|-----|-----|-----|--------|-------|
| Carbon °.....     | 2 | ... | 12  | ... | 8.65                  | ... | 9.00   | } = Methyle | 1          | ... | 15  | ... | 10.63  |       |
| Hydrogen .....    | 3 | ... | 3   | ... | 2.20                  | ... | 2.20   |             |            |     |     |     |        |       |
| Iodine .....      | 1 | ... | 126 | ... | 89.15                 | ... | 88.80  |             | Iodine.... | 1   | ... | 126 | ...    | 89.37 |
| <hr/>             |   |     |     |     |                       |     |        |             |            |     |     |     |        |       |
| Iodide of methyle | 1 |     | 141 |     | 100.00                |     | 100.00 |             |            | 1   |     | 141 | 100.00 |       |

BROMIDE OF METHYLE.  $C_2 H_3 Br, = Me Br$ . This compound is obtained, according to Bunsen, by gently heating bromide of kakodyle, (*Ann. der Pharm.*, XLVI. 44). It is a colorless gas, of a slightly ethereal odor: its density is = 3.155: when cooled to a few degrees below  $0^\circ$ , it condenses into a clear colorless liquid. It is scarcely absorbed by water, or by ether, but abundantly by alcohol; it forms an explosive mixture with oxygen. Its components are

|                    |   |     |    |     |        |             |         |     |     |     |        |
|--------------------|---|-----|----|-----|--------|-------------|---------|-----|-----|-----|--------|
| Carbon .....       | 2 | ... | 12 | ... | 12.90  | } = Methyle | 1       | ... | 15  | ... | 16.12  |
| Hydrogen .....     | 3 | ... | 3  | ... | 3.22   |             |         |     |     |     |        |
| Bromine.....       | 1 | ... | 78 | ... | 83.88  |             | Bromine | 1   | ... | 78  | ...    |
| <hr/>              |   |     |    |     |        |             |         |     |     |     |        |
| Bromide of methyle | 1 |     | 93 |     | 100.00 |             | 1       |     | 93  |     | 100.00 |

FLUORIDE OF METHYLE,  $Me F$ , was obtained by Dumas and Peligot, by distilling sulphate of oxide of methyle with fluoride of potassium. It is a colorless gas, of an ethereal odor; its sp. gr. is 1.186. It burns with a blue flame. Water absorbs nearly 2 volumes of it. (*Ann. Ch. et Ph.*, LXI. 193.)

SULPHURET OF METHYLE.  $C_2 H_3 S = Me S$ . This compound was obtained by Regnault, by distilling sulphate of oxide of methyle with sulphuret of potassium; or by the action of chloride of methyle upon an alcoholic solution of protosulphuret of potassium. It is a liquid of an offensive odor. Its sp. gr. is 0.845 at  $70^\circ$ ; the density of its vapor is 2.11. By the action of chlorine this sulphuret yields a yellow oily compound which, acted upon by excess of chlorine under the influence of light, produces a very fetid volatile liquid, which probably consists of  $C_2 S Cl_3$ . (REGNAULT. *Ann. Ch. et Ph.*, LXX. 391.)

BISULPHURET OF METHYLE.  $C_2 H_3 S_2 = Me S_2$ . This compound was obtained by Cahours (*Ann. Ch. et Ph.*, 3ème Sér., xviii. 257,) by passing chloromethylic gas through an alcoholic solution of bisulphuret of potassium [ $C_2 H_3 Cl, + KS_2, = C_3 H_2 S_2 + KCl$ ], or by distilling a mixture of concentrated solutions of sulphomethylate of lime and bisulphuret of potassium. [ $CaO, C_2 H_3 O_2 SO_3, + KS_2 = KO, SO_3, + CaO,$

SO<sub>3</sub>, + C<sub>2</sub> H<sub>3</sub> S<sub>2</sub>.] The yellow distillate is redistilled, and the portion which passes over between 230° and 250°, is dried by chloride of calcium, and again rectified. This bisulphuret is a transparent colorless and highly refractive liquor, sp. gr. 1·046, boiling between 232° and 234°; the density of its vapor is 3·298: it has a powerful alliaceous odor: it burns with a blue flame: it is scarcely soluble in water, but mixes in all proportions with alcohol and ether.

HYDROSULPHURET OF SULPHURET OF METHYLE. METHYLE-MERCAPTAN. MeS, HS. This compound was obtained by Gregory, by distilling the double sulphate of methyle and potassa, with hydrosulphuret of sulphuret of potassium; these salts were dissolved in a small quantity of water, and heated in a water-bath. [KO, Me O, 2SO<sub>3</sub>] + [HS, KS] = 2[KO, SO<sub>3</sub>] + [Me S, HS]. It is a colorless liquid, lighter than water; it boils at 70°. Its odor is most offensive, resembling that of leeks highly concentrated. It resembles mercaptan in its action upon the oxides of lead and mercury.

COMBINATIONS OF OXIDE OF METHYLE WITH THE ACIDS.

SULPHATE OF OXIDE OF METHYLE. Me O, SO<sub>3</sub>. This compound is obtained by distilling 1 part of wood-spirit with 8 or 10 parts of oil of vitriol; as soon as the mixture boils, a yellow oily liquid passes over, mixed with a thinner fluid; the former, which is the impure sulphate about equals the wood-spirit in bulk; when the whole has distilled over, it is to be washed with water, and then digested upon chloride of calcium, rectified over dry quicklime, and lastly dried under the receiver of the air-pump, with oil of vitriol and caustic potassa included under the same receiver. (DUMAS and PELIGOT.) This sulphate may also be formed by the combination of anhydrous sulphuric acid with gaseous oxide of methyle: the fluid must be rectified over quicklime, and then left for twenty-four hours *in vacuo*, by which it loses a trace of sulphurous acid.

*Sulphate of oxide of methyle* is a colorless oily liquid, of an alliaceous taste and smell. Its sp. gr. is 1·324. It boils at 370°. The density of its vapor is 4·376. It is neutral to test paper, and insoluble in water, which when cold slowly decomposes it: by boiling water it is instantly resolved into wood-spirit and bisulphate. It is not affected by anhydrous lime or baryta; but their hydrates, as well as those of potassa and soda, rapidly decompose it, liberating wood-spirit, and forming a double sulphate of the base and oxide of methyle. Heated with chloride of sodium sulphate of methyle yields chloride of methyle and sulphate of soda: with cyanide of potassium, or of mercury, it produces cyanide of methyle and sulphates of the metallic bases. With formiate of soda the products are sulphate of soda and formiate of oxide of methyle.

The components of this sulphate are

|                              |   |      |    |      |       | Dumas and<br>Peligot. | Regnault.    |
|------------------------------|---|------|----|------|-------|-----------------------|--------------|
| Carbon .....                 | 2 | .... | 12 | .... | 19·3  | .... 19·2             | .... 19·20   |
| Hydrogen.....                | 3 | .... | 3  | .... | 4·8   | .... 4·7              | .... 4·95    |
| Oxygen .....                 | 1 | .... | 8  | .... | 12·5  | } .... 76·1           | } .... 75·85 |
| Sulphuric acid .....         | 1 | .... | 40 | .... | 63·4  |                       |              |
| <hr/>                        |   |      |    |      |       | <hr/>                 | <hr/>        |
| Sulphate of oxide of methyle | 1 |      | 63 |      | 100·0 | 100·0                 | 100·00       |



**BISULPHATE OF OXIDE OF METHYLE. SULPHOMETHYLIC ACID.**  $\text{Me O, HO, 2SO}_3$ . This acid is formed, as already stated, by the action of boiling water upon the neutral sulphate; but it is best obtained by the decomposition of the *sulphomethylate of baryta*, a salt corresponding with the sulphovinate, and prepared by slowly mixing 1 part of wood-spirit with 2 parts of concentrated oil of vitriol; much heat is evolved, and when the mixture has cooled, it is diluted with water, saturated with carbonate of baryta, and filtered. The liquor is then decomposed by the requisite quantity of sulphuric acid, the precipitated sulphate of baryta separated, and the filtrate evaporated, first in a water-bath, and then *in vacuo*.

*Sulphomethylic acid* crystallizes in white needles, soluble in water and in alcohol, and of a very sour taste. It slowly decomposes *in vacuo*, and gives off sulphurous acid; it is more stable when prepared by the action of water upon the neutral sulphate, but when heated is very easily decomposed. It forms an extensive class of salts, *sulphomethylates*, which are almost all crystallizable and soluble in water. When heated they are resolved into sulphates, and sulphate of methyle, the latter being partly decomposed into sulphurous acid, water, &c. These salts, which have been principally examined by Kane, are most readily obtained by decomposing sulphomethylate of baryta by the several sulphates. (*Ann. der Pharm.*, xix. 164.)

**METHYLO-SULPHUROUS ACID.**  $\text{C}_2 \text{H}_3 \text{O, HO, + 2SO}_2$ . This compound, together with its three chloric derivations, was discovered and examined by Kolbe in 1845. (*Ann. der Pharm.*, liv. 174. See also, *Gmelin's Handbuch*. Ed. 1847, iv. 249.)

**NITRATE OF OXIDE OF METHYLE.**  $\text{Me O, NO}_5$ . This compound is formed during the distillation of 50 parts of wood-spirit, 50 of nitre, and 100 of oil of vitriol: the retort must be capacious, and connected with a large receiver communicating with a bottle containing salt and water, and surrounded with ice, from which a tube issues for conveying away the gaseous products. On applying a gentle heat the process commences, and then continues without farther aid. An ethereal liquid condenses in the receiver and in the bottle; and when the process is finished, these are mixed, and the ethereal liquid collects at the bottom of the bottle: it may be separated by decantation, and purified, first by distilling it in a water-bath off a mixture of finely-pulverised litharge and chloride of calcium; and then, rectifying it in a retort furnished with a thermometer: it begins to boil at  $140^\circ$ , but the temperature soon rises to  $150^\circ$ , and then remains stationary: the products are separately collected, inasmuch as the first and more volatile part is contaminated by hydrocyanic acid and other products.

*Nitrate of oxide of methyle* is a colorless liquid of a faint ethereal odor. It burns with a yellow flame. Its sp. gr. is 1.182. It boils at  $150^\circ$ , and furnishes a vapor, the density of which is 2.64, and which is eminently explosive at above  $300^\circ$ . The determination therefore of the density of this vapor is attended by considerable risk. The products of its detonation are nitrous and carbonic acid, and water. This ether is immediately resolved into wood-spirit and nitric acid by the action of a solution of

potassa. The components of this ether are, according to Dumas and Peligot, (*Ann. Ch. et Ph.*, lviii. 41 and lxi. 195,)

|                                      |   |    |       | Dumas and<br>Peligot. |                    |                   |    |        |       |
|--------------------------------------|---|----|-------|-----------------------|--------------------|-------------------|----|--------|-------|
| Carbon .....                         | 2 | 12 | 15.8  | 17.7                  | } Oxide of methyle | 1                 | 23 | 29.87  |       |
| Hydrogen .....                       | 3 | 3  | 3.8   | 4.2                   |                    |                   |    |        |       |
| Oxygen .....                         | 1 | 8  |       |                       |                    |                   |    |        |       |
| Nitric acid .....                    | 1 | 54 | 80.4  | 78.1                  |                    | Nitric acid ..... | 1  | 54     | 70.13 |
| <hr/>                                |   |    |       |                       |                    |                   |    |        |       |
| Nitrate of oxide<br>of methyle ....} | 1 | 77 | 160.0 | 100.0                 |                    | 1                 | 77 | 100.00 |       |

OXALATE OF OXIDE OF METHYLE.  $\text{Me O, C}_2 \text{O}_3$ . This curious compound is prepared by distilling a mixture of equal weights of wood-spirit, oxalic acid, and oil of vitriol, and exposing the distillate to the air, when it deposits the oxalate in the form of crystals, which may be purified by pressure in bibulous paper, and redistillation off oxide of lead. It is then obtained in the form of a white solid transparent substance, composed of rhomboidal tables; it has the odor of oxalic ether. It fuses at  $124^\circ$ , and boils at  $322^\circ$ . It dissolves in, but is soon decomposed by water, and resolved into oxalic acid and wood-spirit. It dissolves in alcohol and in wood-spirit. The alkaline hydrates readily decompose it. Its components are

|                                      |   |     |    |     | Dumas and<br>Peligot. |     |        |       |                     |             |     |     |     |       |
|--------------------------------------|---|-----|----|-----|-----------------------|-----|--------|-------|---------------------|-------------|-----|-----|-----|-------|
| Carbon .....                         | 4 | ... | 24 | ... | 40.67                 | ... | 41.08  | } = { | Oxide of<br>methyle | 1           | ... | 23  | ... | 38.9  |
| Hydrogen .....                       | 3 | ... | 3  | ... | 5.08                  | ... | 5.28   |       |                     |             |     |     |     |       |
| Oxygen .....                         | 4 | ... | 32 | ... | 54.25                 | ... | 53.64  |       |                     | Oxalic acid | 1   | ... | 36  | ...   |
| <hr/>                                |   |     |    |     |                       |     |        |       |                     |             |     |     |     |       |
| Oxalate of oxide of<br>methyle ..... | 1 |     | 59 |     | 100.00                |     | 100.00 |       |                     | 1           |     | 59  |     | 100.0 |

OXAMATE OF OXIDE OF METHYLE. *Oxamethylane*.  $\text{C}_6 \text{H}_5 \text{O}_6 \text{N}$ . This compound was obtained by Dumas and Peligot, by passing a current of dry ammonia over fused oxalo-methylic ether; a white crystalline solid is formed, which, dissolved in boiling alcohol, yields the above substance in iridescent cubic crystals: it may be represented as constituted of 1 atom of oxalate of oxide of methyle, combined with one atom of oxamide, by the formula  $[\text{C}_2 \text{H}_3 \text{O} + \text{C}_2 \text{O}_3] + [\text{C}_2 \text{O}_2 \text{NH}_2]$ .

BISULPHOCARBONATE OF OXIDE OF METHYLE.  $\text{Me O, 2CS}_2$ . When caustic potassa is added to a solution of bisulphuret of carbon in wood-spirit, a salt is obtained  $= \text{C}_6 \text{H}_3 \text{O S}_4, \text{KO}$ . The compound in combination with the potassa, has not been isolated; it has been termed *methyloxanthic acid*. (DUMAS and PELIGOT. *Comptes Rendus*, vi. 20).

BENZOATE OF OXIDE OF METHYLE.  $\text{Me O, C}_{14} \text{H}_5 \text{O}_3$ . This compound is obtained by distilling a mixture of 2 parts of benzoic acid, 2 of sulphuric acid, and 1 of pure wood-spirit, and mixing the distillate with water, when the benzoate falls. The crude product is then washed with water, dehydrated by chloride of calcium, and rectified over oxide of lead. This benzoate is also obtained by the dry distillation of a mixture of benzoate of soda, or of lime, with sulphate of methyle. It is an oily colorless



liquid, of a balsamic odor; insoluble in water, but soluble in alcohol, ether, and wood-spirit: its sp. gr. is 1.10; it boils at 227°; the density of its vapor is 4.75. It consists of

|                                       |                           |       |        |       |                                     |
|---------------------------------------|---------------------------|-------|--------|-------|-------------------------------------|
|                                       | Dumas and<br>Peligot.     |       |        |       |                                     |
| Carbon .....                          | 16....96....70.59....71.4 | } = { |        |       | Oxide of methyle 1.... 23....16.91  |
| Hydrogen .....                        | 8.... 8.... 5.88.... 6.2  |       |        |       | Benzoic acid..... 1....113....83.09 |
| Oxygen.....                           | 4....32....23.53 ...22.4  |       |        |       |                                     |
| <hr/>                                 |                           |       |        |       |                                     |
| Benzoate of oxide of<br>methyle ..... | 1                         | 136   | 100.00 | 100.0 | 1 136 100.00                        |

ACETATE OF OXIDE OF METHYLE. Me O, C4 H3 O3. This acetate is contained in crude wood-spirit. It is best obtained by distilling a mixture of 1 part of concentrated acetic acid, 2 of wood-spirit, and 1 of oil of vitriol: the distillate is mixed with a solution of chloride of calcium, and the light liquor which separates shaken with quicklime, and then left standing for 24 hours upon chloride of calcium to abstract free wood-spirit. It is a colorless liquid of a pleasant ethereal odor, soluble in all proportions in alcohol, ether, and wood-spirit, and in about twice its weight of water. Its sp. gr. is 0.908. It boils at 144°, and the density of its vapor is 2.54. Reichenbach gave the name of *mesite* to a liquid which he extracted from raw pyroxylic spirit, which however proves to be impure acetate of oxide of methyle.

This acetate has been analyzed with the following results:—

|                                      |  |       |        |               |                                 |  |
|--------------------------------------|--|-------|--------|---------------|---------------------------------|--|
|                                      | Weidmann and<br>Dumas and Schweitzer.<br>Peligot. <i>Poggend. Ann.</i> |       |        |               |                                 |  |
| Carbon .....                         | 6...36...48·65...49·15...49·11   | } = { |        |               | Oxide of methyle 1...23...31·16 |  |
| Hydrogen.....                        | 6... 6... 8·10... 8·30... 8·09   |       |        |               |                                 |  |
| Oxygen.....                          | 4...32...43·25...42·55...42·80   |       |        |               |                                 |  |
| <hr/>                                |  |       |        |               |                                 |  |
| Acetate of oxide<br>of methyle ....} | 1  | 74    | 100·00 | 100·00 100·00 | 1 74 100·00                     |  |

MUCATE OF OXIDE OF METHYLE. 2Me O, C12 H8 O14. This compound was discovered by Malaguti, (*Ann. Ch. et Ph.*, Lxiii. 94 and 295), who obtained it as follows. Mucic acid is dissolved in 4 times its weight of sulphuric acid; the solution is at first red and then blackens, and after 12 hours is mixed with 4 parts of wood-spirit, and the mixture left for 24 hours: the concrete mass is then agitated with water, which throws down a crystalline compound, to be purified by solution in and crystallization from alcohol. It forms rhombic prisms. It is not volatile. It dissolves in boiling water, and in 210 parts of boiling alcohol. Its sp. gr. is about 1.5. It does not fuse when heated, but at 325° begins to be decomposed. Its components are

|                                     |                             |       |        |        |                                    |
|-------------------------------------|-----------------------------|-------|--------|--------|------------------------------------|
|                                     | Malaguti.                   |       |        |        |                                    |
| Carbon.....                         | 16.... 96....40.79....40.70 | } = { |        |        | Oxide of methyle 2.... 46 ...19.31 |
| Hydrogen .....                      | 14.... 14.... 5.82.... 5.90 |       |        |        |                                    |
| Oxygen .....                        | 16....128....53.39....53.40 |       |        |        |                                    |
| <hr/>                               |                             |       |        |        |                                    |
| Mucate of oxide of<br>methyle ..... | 1                           | 238   | 100.00 | 100.00 | 1 238 100.00                       |

§ XIX. FORMYLE.  $C_2 H$ . FORMIC ACID.  $C_2 H O_3$ .

When the vapor of *wood-spirit*,  $C_2 H_4 O_2$ , is subjected to the influence of finely-divided platinum, or *platinum-black*, it gives rise to the production of *formic acid*, exactly as alcohol, under the same circumstances, produces acetic acid; but in the present case there is no production of an intermediate compound corresponding to aldehyde. Formic acid is a compound of 3 atoms of oxygen with 1 atom of a hydrocarbon  $= C_2 H$ , to which the term *formyle* has been applied, but which has not been isolated. This hypothetical view of the existence of formyle is convenient, inasmuch as it assimilates the *formylic series* of compounds, with those appertaining to the ethylic, acetylic, and methylic series; it assists the memory in reference to the mutual transmutations or metamorphoses of those compounds, by enabling us to refer them to certain rational formulæ, which in that respect therefore, have a great advantage over the merely empyric formulæ, although the former are generally hypothetical, while the latter represent the result of experiment. In ethyle and acetylene, the atoms of carbon remain constant, and acetylene may be represented as derived from ethyle by the abduction of 2 atoms of its elementary hydrogen,  $C_4 H_6 (= \text{ethyle})$  becoming  $C_4 H_4 (= \text{acetylene})$ . In passing into the methylic and formylic series, ethyle and acetylene lose 2 atoms of carbon; but in methyle and formyle the carbon is again constant,  $C_2 H_4 (= \text{methyle})$  passing, by the abduction of 2 atoms of its elementary hydrogen, into  $C_2 H_2 (= \text{formyle})$ . The relation of these to the olefiant and etherine series will be obvious. In the formyle series the compounds corresponding to ether and to alcohol, namely, the oxide, and its hydrate, are as yet wanting; but with the halogens the series is more complete.

FORMIC ACID.  $C_2 H O_3 + HO = Fo O_3 + HO$ . This acid was originally discovered by Fisher in 1670, in the *red ant* (*Formica Rufa*). (RAY, in *Phil. Trans.*, 1671.) Fourcroy and Vauquelin regarded it as a mixture of acetic and malic acid, (*Annales du Museum*, &c., i. 333; *Phil. Mag.*, xv. 118,) but Suersen, and Gehlen, demonstrated its peculiarities. (*Schweigger's Journal*, iv. 1.) It has subsequently been examined by several eminent chemists. It was formerly obtained by distilling the ants, or their expressed juice, with water (see THOMSON, *Chem. of Inorganic Bodies*, ii. 60, 1831); but other processes are now resorted to for its formation, the principal of which are as follows:—1. Three parts of finely pulverized binocide of manganese are added to a solution of 1 part of sugar in 2 of water; the mixture is heated to  $140^\circ$ , and 3 parts of sulphuric acid are then gradually stirred into it; as soon as the evolution of gas has ceased, it is distilled to dryness. (DÖBEREINER, *Poggend. Ann.*, xxvii. 590. *Ann. der Pharm.*, iii. 141.) 2. Ten parts of starch, 37 of binocide of manganese, 30 of water, and 30 of sulphuric acid, are distilled in a retort (the capacity of which should be at least ten times that of the mixture) till 38 parts have passed over. (LIEBIG, *Ann. der Pharm.*, iii. 207, and xvii. 69.) 3. According to Emmet, the manganese does mischief by resolving formic into carbonic acid: he recommends a mixture of equal bulks of water, sulphuric acid, and the grain of rye, or coarsely



ground maize, to be heated to the boiling-point; when the mixture blackens, he adds an additional volume of water, and then distils over 1 volume of the acid. (*Silliman's American Journ.*, xxxii. 140.) 4. A mixture of 2 parts of tartaric acid, 3 of binocide of manganese, 3 of oil of vitriol, and 3 of water, is gently heated in a large retort, and when the effervescence has ceased, subjected to distillation. (DÖBEREINER.) 5. A mixture of oxalic acid with fine silicious sand is distilled in a glass retort, and the distillate freed from oxalic acid by repeated rectification. This affords a pure and strong formic acid. (GERHARDT, *Ann. Ch. et Ph.*, 3ème Sér., vii. 130.)

These different processes yield a more or less pure and diluted formic acid; in order to obtain it in its most concentrated form, namely, as a *monohydrate*, recourse must be had to the decomposition of *formiate of lead* by sulphuretted hydrogen. To effect this the lead-salt should be dried at about  $260^{\circ}$ , and then introduced in fine powder into a wide glass tube terminating in a smaller one bent at a proper angle; dry sulphuretted hydrogen gas is then passed over the formiate, which should be very gently heated: sulphuret of lead is formed, and the formic acid passes over and may be condensed in a cold receiver; any excess of sulphuretted hydrogen must be expelled from the product by heat. Concentrated formic acid may also be obtained by the distillation of dry formiate of soda with oil of vitriol, but if any excess of the sulphuric acid be used, the formic acid is apt to be decomposed.

*Formic acid* thus obtained is a colorless and slightly fuming liquid, of a pungent odor, and acting as a caustic upon the skin. It congeals at a degree or two below  $32^{\circ}$ . At  $60^{\circ}$  its sp. gr. is 1.235. It boils at about  $210^{\circ}$ , yielding a vapor which burns with a blue flame, and which is resolved into inflammable gases when passed through a red-hot tube. By the catalytic action of finely divided platinum, it is resolved into carbonic acid and water. It reduces the oxides of gold, silver, and mercury, to the metallic state, producing carbonic acid; and if the formic acid be pure, no trace of metal remains in the liquor; but if contaminated by acetic acid, acetate of silver or mercury remains dissolved. Heated with a solution of corrosive sublimate it forms calomel, and hydrochloric and carbonic acids. It acts upon the salts of mercury and silver in the same way as upon their oxides. Heated with metallic peroxides it reduces them to protoxides, which combine with the formic acid, and carbonic acid is at the same time evolved. Chlorine, in the presence of moisture, decomposes formic acid and the formiates, and hydrochloric and carbonic acid are formed.  $C_2 H_2 O_4 + 2Cl = 2CO_2 + 2HCl$ . (CLOEZ, *Ann. Ch. et Ph.*, 3ème Sér., xvii. 297.) Formic acid is rapidly decomposed at a boiling heat by iodic and periodic acid, iodine and carbonic acid being evolved. (BENCKISER, *Ann. der Pharm.*, xvii. 258.) According to Millon the presence of a mere trace of hydrocyanic acid prevents this decomposition. (*Comptes Rendus*, xix. 271.) Sulphuric acid resolves formic acid into carbonic oxide and water; and the formiates are similarly decomposed, with effervescence, but no discoloration.  $C_2 H_2 O_4 = 2HO, 2CO$ .

When 1 atom of the concentrated acid  $= C_2 H O_3 + HO$ , is mixed with an additional atom of water, it remains caustic, but does not crystallize till cooled down to  $5^{\circ}$ : it boils at  $222^{\circ}$ , and its sp. gr. is 1.1004.

(LIEBIG.) Richter gives the following table of the densities and composition of the dilute acid. (LÖWIG, ii. 38.)

|                |      |     |      |     |       |     |      |     |      |     |      |     |       |
|----------------|------|-----|------|-----|-------|-----|------|-----|------|-----|------|-----|-------|
| Sp. gr. ....   | 1.13 | ... | 1.11 | ... | 1.09  | ... | 1.07 | ... | 1.05 | ... | 1.03 | ... | 1.01  |
| Anhydrous acid | 0.46 | ... | 0.30 | ... | 0.316 | ... | 0.29 | ... | 0.15 | ... | 0.10 | ... | 0.033 |

*Anhydrous formic acid* (as it exists in combination with bases) consists of

|                           |   |     |    |     |        | Berzelius. | Göbel. |
|---------------------------|---|-----|----|-----|--------|------------|--------|
| Carbon .....              | 2 | ... | 12 | ... | 32.43  | 32.970     | 32.53  |
| Hydrogen .....            | 1 | ... | 1  | ... | 2.70   | 2.807      | 3.06   |
| Oxygen .....              | 3 | ... | 24 | ... | 64.87  | 64.223     | 64.41  |
| <hr/>                     |   |     |    |     |        |            |        |
| Anhydrous formic acid ... | 1 |     | 37 |     | 100.00 | 100.000    | 100.00 |

The *monohydrated acid* consists of

|                                     |     |     |    |     |        |       |                               |   |     |    |     |        |
|-------------------------------------|-----|-----|----|-----|--------|-------|-------------------------------|---|-----|----|-----|--------|
| Carbon .....                        | 2   | ... | 12 | ... | 26.09  | } = { | Anhydrous formic<br>acid..... | 1 | ... | 37 | ... | 80.43  |
| Hydrogen .....                      | 2   | ... | 2  | ... | 4.35   |       |                               |   |     |    |     |        |
| Oxygen .....                        | 4   | ... | 32 | ... | 69.56  |       |                               |   |     |    |     |        |
| <hr/>                               |     |     |    |     |        |       |                               |   |     |    |     |        |
| Monohydrate of formic<br>acid ..... | } 1 |     | 46 |     | 100.00 |       |                               | 1 |     | 46 |     | 100.00 |

*Formiates.* The affinity of formic acid for bases exceeds that of the acetic acid. (ARVIDSON and OEHREN, *Dissert. de acido formicarum*, Upsal, 1777.) The formiates are obtained by dissolving the bases, or their carbonates, in the hydrated acid, and evaporating. When the formiates of the fixed alkalis are heated to redness in close vessels, they leave carbonates, and evolve carbonic oxide and hydrogen.  $\text{KO}, \text{C}_2\text{H O}_3, = \text{KO}, \text{CO}_2 + \text{CO}, + \text{H}$ . The formiates of zinc, cadmium, cobalt, nickel, copper, lead, and bismuth, leave the pure metal, when heated to redness, evolving water, carbonic acid, and carbonic oxide.  $\text{MO}, \text{C}_2\text{H O}_3 = \text{HO}, + \text{CO}_2, + \text{CO} + \text{M}$ . (GÖBEL. *Schweigger's Journ.*, LXVII. 74, and LXV. 154.) Heated with excess of oil of vitriol the formiates yield sulphates, and water and carbonic oxide are evolved.  $\text{KO}, \text{C}_2\text{H O}_3 + 2\text{SO}_3, = \text{KO}, 2\text{SO}_3, + \text{H O}, + 2\text{CO}$ . When platinum-black is moistened with a solution of an alkaline formiate, it converts it into a carbonate. (DÖBEREINER, *Ann. der Pharm.*, xiv. 14.) The salts of silver and mercury are reduced when boiled in a solution of a formiate. All the formiates are soluble in water, and their aqueous solutions produce a dark orange color with the salts of peroxide of iron. (L. GMELIN.)

*Formiate of Ammonia.*  $\text{NH}_4\text{O}, + \text{Fo O}_3$ . This salt may be formed directly, or by decomposing formiate of lead by carbonate of ammonia; it crystallizes in white plumose prisms, of a pungent taste, and very soluble in water. It fuses at  $248^\circ$ ; at  $284^\circ$  it evolves ammonia, and at  $356^\circ$  is resolved, according to Döbereiner, into hydrocyanic acid and water.  $\text{NH}_4\text{O}, \text{C}_2\text{H O}_3, = \text{C}_2\text{NH} + 4\text{HO}$ . (See also PELOUZE, *Ann. Ch. et Ph.*, XLVIII. 399.)

*Formiate of Potassa.*  $\text{KO}, \text{Fo O}_3$ . This is a difficultly crystallizable anhydrous salt; it is somewhat deliquescent: when heated it first yields undecomposed acid, and then carbonic oxide is evolved till the whole of the acid is decomposed. (GÖBEL.)

*Formiate of Soda.* The crystallized salt is  $\text{NaO}, \text{Fo O}_3, 2\text{HO}$ ; it forms flat rhombic plates and prisms; its taste is saline and bitter: when



heated it first fuses in its water of crystallization, and then concretes into a dry mass which deliquesces in damp air.

*Formiate of Lime*,  $\text{Ca O}$ ,  $\text{Fo O}_3$ , crystallizes, according to Göbel, in transparent truncated octohedra, efflorescent, and of a saline bitter taste; soluble in 10 parts of water; insoluble in alcohol.

*Formiate of Baryta*.  $\text{Ba O}$ ,  $\text{Fo O}_3$ . This is an anhydrous salt, crystallizing in transparent prisms, soluble in 4 parts of cold water, but insoluble in alcohol; its components are

|                    |   |      |     |      |        | Richter. |        | Gehlen. |        | Göbel.     |
|--------------------|---|------|-----|------|--------|----------|--------|---------|--------|------------|
| Baryta .....       | 1 | .... | 77  | .... | 67.55  | ....     | 68.56  | ....    | 68.75  | .... 67.74 |
| Formic acid .....  | 1 | .... | 37  | .... | 32.45  | ....     | 31.44  | ....    | 31.25  | .... 32.26 |
| <hr/>              |   |      |     |      |        |          |        |         |        |            |
| Formiate of baryta | 1 |      | 114 |      | 100.00 |          | 100.00 |         | 100.00 | 100.00     |

*Formiate of Magnesia*,  $\text{Mg O}$ ,  $\text{Fo O}_3$ , forms anhydrous acicular crystals soluble in 13 parts of cold water, but insoluble in alcohol. (*Acetate* of magnesia is readily soluble in alcohol.) They consist of

|                            |   |      |    |      |        |      | Richter. |      | Göbel. |
|----------------------------|---|------|----|------|--------|------|----------|------|--------|
| Magnesia .....             | 1 | .... | 20 | .... | 35.09  | .... | 37.58    | .... | 35.55  |
| Formic acid .....          | 1 | .... | 37 | .... | 64.91  | .... | 62.42    | .... | 64.44  |
| <hr/>                      |   |      |    |      |        |      |          |      |        |
| Formiate of magnesia ..... | 1 |      | 57 |      | 100.00 |      | 100.00   |      | 100.00 |

*Formiate of Manganese*.  $\text{Mn O}$ ,  $\text{Fo O}_3$ . This salt was obtained by dissolving carbonate of manganese in the acid; it forms reddish efflorescent tabular crystals (ARVIDSON), small prisms (GÖBEL), soluble in 15 parts of cold water, but insoluble in alcohol.

*Formiate of Protoxide of Iron*.  $\text{Fe O}$ ,  $\text{Fo O}_3$ . This salt cannot, according to Göbel, be obtained in crystals. The filtrate obtained from a solution of formiate of baryta decomposed by protosulphate of iron, deposits a yellow basic persalt when evaporated under exposure to air. (LIEBIG.) Hydrated peroxide of iron is only sparingly soluble in formic acid, and leaves a brown deliquescent crystalline mass.

*Formiate of Zinc*,  $\text{Zn O}$ ,  $\text{Fo O}_3$ ,  $2\text{HO}$ , forms cubic crystals, sparingly soluble in water, and insoluble in alcohol. (Soluble in 24 parts of water at  $60^\circ$ . GÖBEL.) When oil of turpentine is kept in zinc canisters, small white granular crystals are formed in them, which, when purified by ether and alcohol, are found to be formiate of zinc: they also contain 2 atoms of water. (LAURENT.)

*Formiate of Tin*. The oxides of tin do not appear to form permanent or definite combinations with formic acid. (GÖBEL.) A mixture of bichloride of tin and formiate of soda becomes white and gelatinous when heated, and a crystalline precipitate is gradually formed. (LIEBIG.)

*Formiate of Cadmium*,  $\text{Cd O}$ ,  $\text{Fo O}_3$ ,  $2\text{HO}$ , crystallizes in cubes and rhombic dodecahedra, very soluble, and of a sweetish metallic taste. (GÖBEL.)

*Formiate of Copper*,  $\text{Cu O}$ ,  $\text{Fo O}_3$ ,  $4\text{HO}$ , crystallises in blueish-green six-sided prisms, efflorescent, and soluble in 8.5 of cold water. When decomposed by heat they leave metallic copper.

*Formiate of Lead*.  $\text{Pb O}$ ,  $\text{Fo O}_3$ . When formic acid is added to a saturated solution of acetate of lead, brilliant acicular crystals are gradually formed; and if the formic acid be in excess, the liquor solidifies. The crystals may be purified by washing them with water. They are

anhydrous, and dissolve in about 40 parts of cold water. The sparing solubility of this salt renders it available as a test of formic acid; and its insolubility in alcohol furnishes a means of separating formic from acetic acid. The solution of formiate of lead is sweet: when boiled with excess of oxide of lead it assumes an alkaline reaction. (LIEBIG.)

The components of this salt are

| Berzelius. Göbel.  |       |         |           |           | Lecanu. |       |  |                            |
|--------------------|-------|---------|-----------|-----------|---------|-------|--|----------------------------|
| Oxide of lead....  | 1.... | 112.... | 75·17.... | 74·88.... | 75·50   | } = { | Oxide<br>of lead }<br>Formic<br>acid } | 1....112....75·17....74·88 |
| Carbon .....       | 2.... | 12....  | 8·05....  | 8·28....  | 7·97    |       |  |                            |
| Hydrogen .....     | 1.... | 1....   | 0·67....  | 0·71....  | 0·75    |       |  |                            |
| Oxygen .....       | 3.... | 24....  | 16·11.... | 16·13.... | 15·78   |       |  |                            |
| Formiate of lead 1 | 149   | 100·00  | 100·00    | 100·00    |         |       |  | 1 149 106·00 100·00        |

*Formiate of Suboxide of Mercury.*  $\text{Hg}_2\text{O}$ ,  $\text{Fo O}_3$ . When oxide of mercury (peroxide) is digested in cold aqueous formic acid, containing 10 *per cent.* of anhydrous acid, the solution effervesces when gently heated, from the escape of carbonic acid, and deposits brilliant acicular crystals. At first a solution of the formiate of the peroxide is formed, which is decomposed when heated, 4 atoms of it being resolved into 2 atoms of formiate of the suboxide, 1 atom of free formic acid, and 2 atoms of carbonic acid.  $4 [\text{C}_2\text{H HgO}_4] = 2 [\text{C}_2\text{H Hg}_2\text{O}_4] + [\text{C}_2\text{H}_2\text{O}_4] + 2 [\text{CO}_2]$ . Inasmuch as formic acid is here set free, the liquor which has deposited the crystals of the salt of the suboxide, may be again saturated in the cold with oxide of mercury, and when gently heated will afford a second portion of the suboxide salt. If the solution of the oxide be too highly heated, mercury is set free, which renders the crystals grey; and on continuing the heat, metallic mercury falls, and no crystals are formed. (L. GMELIN.) The crystals of the suboxide-salt may be dried between folds of bibulous paper at a temperature of about  $90^\circ$ ; they feel greasy, and taste metallic and astringent. They blacken, especially when moist and exposed to light. When rubbed, or when heated to  $212^\circ$ , they are resolved into mercury, carbonic acid, and formic acid.  $2 [\text{Hg}_2\text{O}, \text{C}_2\text{H O}_3] = 4\text{Hg} + 2\text{CO}_2 + \text{C}_2\text{H O}_3$ .] When the aqueous solution of this salt is boiled, mercury is gradually deposited, carbonic acid evolved, and formic acid remains in the liquor. The crystals dissolve in 520 parts of water at  $62^\circ$ , but are more soluble in hot water. They are insoluble in alcohol and in ether. They consist of

|                                       |   |     |     |     |        |     | Göbel. |
|---------------------------------------|---|-----|-----|-----|--------|-----|--------|
| Suboxide of mercury .....             | 1 | ... | 208 | ... | 84·9   | ... | 83·168 |
| Formic acid.....                      | 1 | ... | 37  | ... | 15·1   | ... | 16·832 |
| Formiate of suboxide of mercury ..... | 1 |     | 245 |     | 100·00 |     | 100·00 |

*Formiate of Red Oxide of Mercury.* When this oxide is dissolved in cold and very dilute formic acid, the solution at first yields a yellow precipitate with potassa, and a white one with ammonia. Evaporated *in vacuo* over oil of vitriol, it leaves a white granular salt, soluble in water, which upon the slightest application of heat gives off carbonic acid and deposits the acicular crystals of the formiate of the suboxide. (GÖBEL. LIEBIG.)

*Formiate of Silver.* When concentrated solutions of neutral nitrate of silver, and of slightly acid formiate of potassa are mixed, a white crystalline precipitate falls, which soon blackens in the light, and which when



heated, is resolved into metallic silver, carbonic acid, and formic acid. Oxide of silver is not soluble in, but immediately reduced by, hot formic acid. (GÖBEL. LIEBIG.)

CHLORIDES, IODIDES, AND BROMIDES OF FORMYLE. Several of the compounds to which some have assigned these names have already been described under the combinations of hydrocarbons, or of ethyle, acetylene, or methyle. They have chiefly been examined by Regnault, (*Ann. Ch. et Ph.*, LXXI. 353,) whose researches connected with them have been repeatedly quoted. It is obvious that the acetylic, methylic, and formylic compounds may all be derived from the ethylic series, either by the abstraction of hydrogen, or of hydrogen and carbon; and that the rational formulæ assigned to them will vary, according as olefiant gas, or ethylene, or ethyle, are regarded as the radical. *Chloroform*, which has already been noticed as a derivative of alcohol (p. 1704), is perhaps one of the least equivocal of the formylic compounds, inasmuch as it is represented by  $C_2HCl_3$ , or  $ForCl_3$  (formic acid being  $ForO_3$ ): but even to that substance the formula  $C_2HCl_2$  has been by some assigned, and it has been transferred from the formylic to the methylic series, although alcoholic solution of potassa decomposes it with the production of formiate of potassa and chloride of potassium.  $C_2HCl_3 + 4KO = KO, C_2HO_3 + 3KCl$ .

TERIODIDE OF FORMYLE.  $ForI_3$ . This compound, called also *iodoform*, has been already mentioned (p. 1706). It is best obtained by boiling in a long-necked flask a mixture of 60 grains of iodine, 50 of carbonate of potassa, and 60 of alcohol diluted with 3 parts of water: the boiling is continued till the color of the iodine has disappeared; on diluting with water the teriodide falls, and only requires washing with water. (MOHR, *Ann. der Pharm.*, xxix. 12.)

Teriodide of formyle may be obtained in yellow nacreous crystals by the spontaneous evaporation of its solution in alcohol; it has a strong saffron-like odor; it is insoluble in water, but readily soluble in alcohol and in ether. It fuses, and then sublimes, at about  $212^\circ$ . It is decomposed by an alcoholic solution of potassa, into iodide of potassium and formiate of potassa.  $ForI_3 + 4KO = KO, ForO_3 + 3KI$ .

When teriodide of formyle is distilled with perchloride of phosphorus, a red liquid passes over, which, rectified over sulphuric acid, yields a yellow fluid, sp. gr. 1.69. Its components are  $C_2HI_2$ . (SERULLAS. *Poggend. Ann.*, xv. 72. BOUCHARDAT. *Journ. de Pharm.*, xi. 18.)

TERBROMIDE OF FORMYLE,  $ForBr_3$ , or *Bromoform*, is best obtained by distilling diluted alcohol, wood-spirit, or acetone, with bromide of lime: it closely resembles chloroform, but it is more easily decomposed by the alkalis, and its specific gravity is higher, being 2.10. (DUMAS.)<sup>a</sup>

TERSULPHURET OF FORMYLE. SULFOFORM.  $ForS_3$ . This compound is obtained, according to Bouchardat (*Ann. der Pharm.*, xxii. 234), by carefully distilling in a small retort, a mixture of 1 part of teriodide of formyle, and 3 parts of finely pulverised cinnabar: Iodide of mercury is formed, and a dense oleaginous liquor passes over, which is heavier than oil of vitriol, and of a sweetish aromatic, but at the same time sulphur-

ous odor. It is soluble in alcohol and in ether. By the action of potassa it affords formiate of potassa, and sulphuret of potassium:  $\text{Fo S}_3 + 4\text{KO} = \text{KO}, \text{Fo O}_3 + 3\text{KS}$ .

OXICHLORIDE OF FORMYLE.  $\text{C}_2 \text{H Cl}_2 \text{O} = \text{FoO}, \text{Cl}_2$ . This compound was obtained by Regnault (*Ann. Chim. et Ph*, Lxxi. 353), as a product of the action of chlorine upon gaseous oxide of methyle under the influence of light (but not of direct sunshine). The first result is a compound  $= \text{C}_2 \text{H}_2, \text{Cl}, \text{O}$ , which he calls *monochloruretted methylic ether*; it is a very mobile liquid, of a suffocating odor, very irritating to the eyes and nose, and giving off acid fumes when exposed to moist air. Its sp. gr. is 1.315, at  $68^\circ$ ; it boils at  $220^\circ$ , and the density of its vapor is 4.04. When this compound is exposed in an atmosphere of chlorine to the further action of light, it is converted into *oxichloride of formyle*, (called by Regnault *bichloruretted methylic ether*), hydrochloric acid being at the same time formed:  $\text{C}_2 \text{H}_2 \text{Cl O} + 2\text{Cl}$ , becoming  $\text{C}_2 \text{H Cl}_2 \text{O} + \text{HCl}$ .

Oxichloride of formyle is a pungent irritating compound, but of a less powerful odor than the above-mentioned combination, like which it gives off acid fumes in the atmosphere. Its sp. gr. is 1.6 at  $68^\circ$ ; it boils at  $266^\circ$ , and the density of its vapor is 6.36.

Under the further influence of chlorine and sunshine, this substance is deprived of the whole of its hydrogen, and passes into  $\text{C}_2 \text{Cl}_3 \text{O}$ , a compound called by Regnault *perchloruretted methylic ether*: it has a strong penetrating odor; its sp. gr. is 1.59; it boils at about  $212^\circ$ , and the density of its vapor is 4.67. As explosions sometimes occur in the production of the preceding compounds, the precautions pointed out by Regnault in the memoir which I have quoted, should be attended to.

## § XX. AMYLIC ALCOHOL. HYDRATE OF OXIDE OF AMYLE.



This compound has long been known under the name of *oil of potato-spirit*; it is the *fusel oil* of the Germans. It was first examined by Pelletan, (*Ann. Ch. et Ph.*, xxx. 221), and afterwards by Dumas, (*ibid.*, lvi. 314), and more especially by Cahours, (*ibid.*, lxx. 81; and lxxv. 193). It is now considered as the *alcohol* of the *amyllic series*, the base of which, or *amyle*,  $= \text{C}_{10} \text{H}_{11}$ , has not as yet been isolated. It has hitherto been exclusively obtained as a product of fermentation, especially from potato-brandy. Balard (*Erdmann and Marchand's Journ.*, xxxiv. 123), has found it, accompanying cœnanthic ether, in the volatile oil obtained from brandy; it has also been detected in the spirit afforded by the fermentation of beet-root treacle. It is abundantly obtained from corn-spirit, in the process of its rectification upon the large scale.

HYDRATE OF OXIDE OF AMYLE. AMYLIC ALCOHOL.  $\text{Ayl O}, \text{HO}$ . When potato-brandy is distilled, and after the greater part of the alcohol has passed over, a milky liquid is obtained, which deposits the crude *potato-oil*. It is similarly obtained among the less volatile products of the distillation of corn-spirit of all kinds. This crude oil is purified by washing it with water, and then drying it by means of chloride of calcium, and redistilling it; the portion which passes over at about  $268^\circ$  or  $270^\circ$ , is pure *hydrate of oxide of amyle*.





**IODIDE OF AMYLE.** *Ayl I.* This compound is obtained by heating a mixture of 8 parts of iodine, 1 of phosphorus, and 15 of amylic alcohol; the product, after having been washed with water, and dehydrated by chloride of calcium, is redistilled. It is a heavy colorless liquid, volatile at  $248^{\circ}$ ; it has a pungent taste, and an alliaceous odor; when heated its vapor burns with a purple flame. The density of its vapor is 6.82. It is decomposed when exposed to light, and iodine is set free. It is immediately decomposed by an alcoholic solution of potassa. It consists of

|                 |    |     |     |     | Calours.                          |     |        |  |
|-----------------|----|-----|-----|-----|-----------------------------------|-----|--------|--|
| Carbon .....    | 10 | ... | 60  | ... | 30.83                             | ... | 30.96  |  |
| Hydrogen .....  | 11 | ... | 11  | ... | 5.53                              | ... | 5.25   |  |
| Iodine .....    | 1  | ... | 126 | ... | 63.64                             | ... | 63.79  |  |
|                 |    |     |     |     | }                                 |     |        |  |
|                 |    |     |     |     | = {                               |     |        |  |
|                 |    |     |     |     | Amyle .... 1 .... 71 .... 36.21   |     |        |  |
|                 |    |     |     |     | Iodine .... 1 .... 126 .... 63.79 |     |        |  |
| Iodide of amyle | 1  |     | 197 |     | 100.00                            |     | 100.00 |  |
|                 |    |     |     |     | }                                 |     |        |  |
|                 |    |     |     |     | 1 197 100.00                      |     |        |  |

**BROMIDE OF AMYLE,** *Ayl Br*, is obtained in the same way as the iodide; it also is a heavy colorless liquid of an alliaceous and pungent smell and taste. It burns difficultly with a green flame. It is readily decomposed by alcoholic solution of potassa. It consists of

|                  |    |     |     |     | Calours.                       |     |        |  |
|------------------|----|-----|-----|-----|--------------------------------|-----|--------|--|
| Carbon .....     | 10 | ... | 60  | ... | 41.69                          | ... | 41.79  |  |
| Hydrogen .....   | 11 | ... | 11  | ... | 7.47                           | ... | 7.55   |  |
| Bromine .....    | 1  | ... | 78  | ... | 50.84                          | ... | 50.66  |  |
|                  |    |     |     |     | }                              |     |        |  |
|                  |    |     |     |     | = {                            |     |        |  |
|                  |    |     |     |     | Amyle.... 1 .... 71 .... 49.16 |     |        |  |
|                  |    |     |     |     | Bromine 1 .... 78 .... 50.84   |     |        |  |
| Bromide of amyle | 1  |     | 149 |     | 100.00                         |     | 100.00 |  |
|                  |    |     |     |     | }                              |     |        |  |
|                  |    |     |     |     | 1 149 100.00                   |     |        |  |

**AMYLCHLORAL.** **CHLORAMYLAL.**  $C_{20}H_{17}O_4Cl$ . A compound having the preceding formula, is obtained by passing dry chlorine through purified potato-oil, washing the product, then dehydrating it by chloride of calcium, and distilling: it is a yellow oily liquid, having a taste slight at first, but afterwards acrid. It is insoluble in water, but soluble in alcohol and in ether. It boils at  $356^{\circ}$ . (CAHOURS.)

**SULPHURET OF AMYLE.** *Ayl S.* Balard obtained this compound by saturating an alcoholic solution of sulphuret of potassium with chloride of amyle, leaving the mixture for some time in a close vessel at a high temperature, and then distilling it. The product has a strong odor and flavor of onions; its sp. gr. is 0.87; it boils at  $420^{\circ}$ , the density of its vapor being 6.3. Its elements are

|                        |    |     |    |     | Balard.                         |     |       |  |
|------------------------|----|-----|----|-----|---------------------------------|-----|-------|--|
| Carbon.....            | 10 | ... | 60 | ... | 68.9                            | ... | 68.2  |  |
| Hydrogen .....         | 11 | ... | 11 | ... | 12.6                            | ... | 12.6  |  |
| Sulphur .....          | 1  | ... | 16 | ... | 18.5                            | ... | 19.2  |  |
|                        |    |     |    |     | }                               |     |       |  |
|                        |    |     |    |     | = {                             |     |       |  |
|                        |    |     |    |     | Amyle .... 1 .... 71 .... 81.5  |     |       |  |
|                        |    |     |    |     | Sulphur.... 1 .... 16 .... 18.5 |     |       |  |
| Sulphuret of amyle.... | 1  |     | 87 |     | 100.0                           |     | 100.0 |  |
|                        |    |     |    |     | }                               |     |       |  |
|                        |    |     |    |     | 1 87 100.0                      |     |       |  |

**HYDROSULPHURET OF SULPHURET OF AMYLE.** **AMYLMEERCAPTAN.** *Ayl S, HS.* This compound, first obtained by Krutsch, (*Erdmann and Marchand's Journ.*, xxxi. 1.) is formed as follows: an aqueous solution of sulphamylic acid is mixed with potassa and saturated with sulphuretted hydrogen; it is then distilled in a chloride of lime-bath to prevent bumping, and the amyle compound removed by a pipette from the watery



product; it is then dehydrated by chloride of calcium and redistilled. Balard obtains it by the decomposition of an alcoholic solution of hydrosulphuret of sulphuret of potassium by chloride of amyle, and subsequent distillation: on mixing the distillate with water, the amymercaptan floats upon the surface.

Amylmercaptan is a highly refractive oily liquid, of a penetrating garlic odor; its sp. gr. is 0·835; its boiling-point about 250°, and the density of its vapor 3·6. By the action of nitric acid, it is converted into a coupled acid,  $=\text{Ayl} \left\{ \begin{smallmatrix} \text{S} \\ \text{O} \end{smallmatrix} \text{SO}_3 + \text{HO} \right.$ , the properties, and several of the salts of which, have been described by Gerathewohl (*Erdmann and Marchand's Journ.*, xxxiv. 447. Löwig, *Chem. d. Org. verb.*, ii. 486.) The components of amymercaptan are

| Krutsch.                                  |    |     |       |        |              |   |   |
|---|----|-----|-------|--------|--------------|---|---|
| Carbon .....                              | 10 | 60  | 57·6  | 57·51  | }            | = | { |
| Hydrogen .....                            | 12 | 12  | 11·5  | 11·51  |              |   |   |
| Sulphur.....                              | 2  | 32  | 30·9  | 30·98  |              |   |   |
| <hr/>                                     |    |     |       |        | <hr/>        |   |   |
| Hydrosulphuret of<br>sulphuret of amyle } | 1  | 104 | 100·0 | 100·00 |              |   |   |
|   |    |     |       |        | 1 104 100·00 |   |   |

surface, and may be removed and rectified. It is also formed during the violent action which ensues when a mixture of nitric acid and amylic alcohol is gently heated; it must be condensed in a cooled receiver, and distilled off potassa, by which the hydrocyanic acid it contains is decomposed; what passes over at  $205^{\circ}$ , is the pure product. It is a pale yellow liquid, boiling at  $205^{\circ}$ , and yielding a yellowish vapor, the density of which is 4.07. (BALARD).

OXALATE OF OXIDE OF AMYLE,  $\text{Ayl O, C}_2\text{O}_3$ , is obtained by heating amylic alcohol with excess of oxalic acid; an oil-like liquid gradually separates, which is *almylo-oxalic acid*, and which, distilled at  $500^{\circ}$ , yields the above oxalate: its sp. gr. is 0.85; that of its vapor is 7.9: it has the odor of bugs.

BORATE OF OXIDE OF AMYLE.  $\text{Ayl O, 2BO}_3$ . This compound has been described by Ebelmen. (*Ann. Ch. et Ph.*, 3ème Sér., xvi. 129,) 2 parts of amylic alcohol and 1 of boracic acid were heated in a retort up to  $356^{\circ}$ ; nothing passed over, but on digesting the contents of the retort in anhydrous ether, evaporating the ethereal solution, and heating the residue to about  $500^{\circ}$ , the boric compound remains: it is a glossy substance, which sustains a temperature of  $570^{\circ}$ , without decomposition; at a higher temperature it is decomposed, and leaves fused boracic acid.

SILICATE OF OXIDE OF AMYLE has also been described by Ebelmen; he obtained it by the action of chloride of silicium on amylic alcohol: it much resembles the corresponding silicate of oxide of ethyle.

ACETATE OF OXIDE OF AMYLE.  $\text{Ayl O, AcO}_3$ . This compound is formed by distilling a mixture of 2 parts of acetate of potassa, 1 of amylic alcohol, and 1 of sulphuric acid; the distillate after having been washed with alkaline water, is dehydrated by chloride of calcium, and rectified over oxide of lead. (CAHOURS.) The product is a very transparent, colorless, volatile liquor, of an ethereal odor; it is lighter than and insoluble in water, but soluble in alcohol and ether. It boils at  $248^{\circ}$ .

VALERATE OF OXIDE OF AMYLE. This compound is produced, together with valeric acid, by the action of a mixture of chromate of potassa and sulphuric acid upon amylic alcohol, as described at p. 1556.

Amylic alcohol has the same relation to valeric acid, that alcohol has to acetic acid, and methylic alcohol to formic acid; and when it is subjected in the contact of air to the action of platinum-black, so as to form water and valeric acid, it is probable that in the first instance a compound corresponding to aldehyde is formed.

AMYLENE.  $\text{C}_{10}\text{H}_{10}$ . When amylic alcohol is distilled with anhydrous phosphoric acid, a colorless oily liquid passes over; it is lighter than water; its boiling point is about  $320^{\circ}$ . It is a hydrocarbon isomeric, with olefiant gas, and etherine, but the density of its vapor is 5.06, which is 5 times that of olefiant gas; each volume of it therefore contains 10 volumes of hydrogen, in combination with 10 atoms of carbon; its equivalent is 70. (CAHOURS.)



## CHAPTER VIII.

## ANIMAL PRODUCTS.

THE ultimate elements of animal substances are the same as those of vegetables, namely, carbon, hydrogen, oxygen, and nitrogen; but nitrogen, sulphur, and phosphorus, are more generally and abundantly present. The processes resorted to for the quantitative determination of these ultimate elements have been already fully described (p. 1150, &c.), except, perhaps, as regards sulphur and phosphorus, respecting which some details will be found in the sequel.

The humidity of the proximate components of animals, their organization, and their ultimate composition, are such, as in many cases to render them extremely prone to change, after the loss of vitality; and the very circumstances which contribute to their permanence and stability whilst under the influence of life, are, apparently, those, which after death, render them particularly susceptible of decomposition. The putrefaction of animal substances is distinguished from that of most vegetables, by the nauseous stench which attends it, partly arising from the presence of sulphur and phosphorus in the gaseous products, and partly from other combinations, with the exact chemical nature of which we are unacquainted.

The *solids of animals* derive their soft, flexible, or elastic texture, partly from their peculiar retentive power in regard to water; for, though not wet or moist, in the common acceptation of the term, they sometimes contain four-fifths of their weight of water, part of which may be squeezed out or dried off, when they become hard, brittle, or translucent, but again swell up and regain their former appearance on being immersed in water: this desiccation, however, always kills the part, if we perhaps except some among the lower orders of the animal creation, which are said to admit of being dried, and again revive when moistened. Under this view of the subject, therefore, a living animal may be regarded as a mass of organized and organic matter, softened by water, probably to the amount of about three-fourths of its total weight. It has been ascertained that nothing but pure water gives the peculiar flaccidity and softness to which I have alluded: salt water, spirits, oils, and all other liquids, producing very different effects. When microscopically examined, these soft solids generally appear to be made up of small globular particles.

When the organized textures of animals are subjected to *destructive distillation*, *ammonia* is a leading product; it is generally more or less saturated by carbonic, and occasionally by other acids, and often in the state of solid carbonate, or dissolved in water and contaminated by empyreumatic oil; the *salt* and *spirit of hartshorn* of old pharmacy, are products of this description, and the same are afforded by common bone, provided the *fat* has been previously separated; for fat yields distinct products, being destitute of nitrogen. The *empyreumatic oil* formed in these processes, and often termed *Dippel's oil*, first passes over of a pale-yellow color; it gradually becomes darker and thicker; but when redistilled

with water, it is nearly colorless, of a penetrating odor, and gradually acquires a brown color by exposure to air; it is alkaline, soluble in alcohol, inflamed by nitric acid, and by somewhat diluted nitric acid becomes resinous: it is soluble in hydrochloric acid, and precipitated by sulphuric and nitric acids; and by alkalis in an altered and apparently resinous state. The *tar* associated with this oil, has been before noticed as a source of *eupion* (p. 1212). This, and the oil, have been examined by Unverdorben, who has found in them no less than four distinct substances, which he considers as *salifiable bases*; namely, 1. *Odorin* (from *odor*), obtained by saturating the ammonia in the rectified oil, by nitric acid, then pouring off the oil, and distilling it in a water-bath; the first portion which passes over is *odorin*; it has the concentrated odor of *Dippel's oil*, and combines with the acids, forming peculiar oily salts; it also forms double salts, in conjunction with several other salifiable bases. 2. *Animin* (from *animal*), is contained in the oil which succeeds the odorin; this, washed with water, saturated with sulphuric acid, and distilled, leaves *animin*; it is an oily fluid, having the odor of purified salt of harts-horn. 3. *Olanin* (from the first syllables of *oleum animale*), remains in the retort after the odorin and animin have distilled over; when washed with water, it resembles a fat oil; and when exposed to air it becomes brown, and is converted into *fuscin*. 4. *Ammolin* (from the first syllables of *ammonia* and *oleum*), is obtained from the crude or unrectified animal oil. Unverdorben has also described another salifiable base, which he obtains from animal empyreumatic oil, and which, as it forms crystallizable compounds with the acids, he has termed *krystallin*. The details of these researches, which are complicated, are contained in *Poggendorf's Journal* (viii. and xi.), and abstracts of them are given by Berzelius and Gmelin: it appears probable, that some of the supposed *educts* are produced by the various processes to which the oil is submitted for their separation; those who are engaged in researches connected with this subject, must consult the original papers.

The *gaseous products* of the destructive distillation of animal matter are extremely various, and easily modified in quality as well as quantity, by the manner in which the process has been conducted; the *charcoal* which remains after the separation of the volatile principles, has been already repeatedly noticed as peculiarly adapted to the removal of color, odor, and taste, from various solutions; and in consequence of the salts which it contains, and especially the phosphates, it resists incineration, and requires particular management when its incombustible contents are to be separated.

**PUTREFACTION AND PRESERVATION OF ANIMAL MATTER.** The phenomena of animal putrefaction are extremely varied and complicated, and are easily affected by extraneous causes, such as temperature, air, moisture, and other agents. The changes which are thus produced in individual parts of animals are elsewhere mentioned, but a few general observations may be made here, in reference chiefly to circumstances which influence or modify the process.

The influence of *temperature* is commonly known; every one is acquainted with the preservative powers of *cold*; when animal matters are subjected to higher temperatures than those of warm climates, they



undergo changes which do not come within the meaning of the term *putrefaction*. The greater number of animal substances are indefinitely preserved, at, or below the freezing-temperature, and when slowly thawed, they generally regain their original characters; it is in this way that supplies of animal food are kept in a fresh state in many parts of the north of Europe, and that fish is preserved for the London market. A remarkable instance of the preservative power of cold was exhibited in the ancient elephant, found incased in a mass of ice, at the mouth of the river Lena, in Siberia. (*Mém. Imp. Acad. St. Petersb.*, V. *Quart. Journ. of Science*, &c., viii. 95, 1820.) The Laplanders preserve rein-deers' milk in a frozen state, and when thawed, after the lapse of several months, it perfectly retains its original characters. (VON BUCH.)

*Moisture* is another essential to putrefaction; when flesh is carefully and thoroughly dried, either by a current of warm and dry air, or by other methods which do not alter its composition, it resists decay; it has thus occasionally happened that corpses have been preserved by accidental desiccation; and animal substances which are either naturally dry, or rendered so by art, retain their nutritive powers, and resume their former appearance when cautiously moistened. The various forms of gelatine, whilst kept dry, are imperishable; whilst in aqueous solution, or in their original humid state, they are the most perishable of the animal proximate principles, as skin, and the varieties of tremulous jelly, show.

*Air*, or at least *oxygen*, if not absolutely essential to, is a powerful promoter of putrefactive changes, and under certain circumstances, its exclusion indefinitely retards them. Hence, the rapidity of putrefactive changes in pure oxygen, and their retardation in gases which either do not contain it, or in which it is held by superior attractive power. Even under water, when oxygen is strictly excluded, putrefaction is greatly retarded and modified in its results. Meat immersed in water previously boiled to expel air, and then covered by a layer of oil, to prevent its subsequent absorption, may long be kept fresh: the presence of iron-filings and of sulphur in the water, assist in this species of preservation.

In Appert's method of preserving animal and vegetable food, the substances are hermetically sealed in tin canisters, and then par-boiled; the included oxygen becomes converted into carbonic acid, or enters into other combinations. The best mode of conducting this process consists in introducing the partially boiled or roasted meat, or half-dressed vegetables, soup, &c., into the canister, which is then soldered up, with the exception of a small hole left in the lid: the canisters are then placed in a saline bath, heated a few degrees above the boiling-point of water, and when steam is copiously issuing from the aperture, it is dexterously soldered up; so that the canister is not only hermetically sealed, but a vacuum created within it: it of course requires to be strong enough to resist atmospheric pressure. Oil, butter, suet, and such substances, are sometimes similarly effectual; and potted and preserved meats, when covered with a film of fatty matter, itself not prone to change, are in that way preserved from the contact of air.

The manner in which various *saline substances*, and especially common salt, act, is not very clearly understood; it is partly by desiccation, or abstraction of moisture, and by a corrugating power over the animal

fibre; and partly by the production of new compounds arising out of the action of the salt employed, or its elements, upon the organic matter: the preservative powers of corrosive sublimate, sulphate of zinc and of copper, acetate of copper, the corresponding salts of iron, and very many other similar compounds, are of the same description. These *anti-putrefactives* are generally coagulators of albumine, and alcohol, kreasote, and some of the dilute acids, have the same power, and are also effective preservatives. For the preservation of bodies for the purposes of dissection, a solution of sulphite of soda injected into the blood-vessels has been found very effectual. Among vegetable products, the various forms of tannine act apparently by direct union with the animal fibre, producing combinations which are insoluble in water, which resist the joint agency of air and moisture, and which admit of desiccation. Sugar, which is sometimes employed as a substitute for salt, acts apparently by its affinity for water; and meat, which has been deprived by these or other means of only a part of its water, becomes infinitely less susceptible of putrefactive changes. Sugar has been found very effectual in the preservation of milk, an article to which Appert's method was never successfully applicable. When milk, with the addition of a certain quantity of sugar, is carefully evaporated at a low temperature to a pasty consistence, and in that state hermetically sealed in a proper canister, it may be long kept, and affords, when diluted with warm water, a solution not distinguishable from sweetened fresh milk.

The ancient Egyptians seem to have availed themselves of almost all these methods of preservation in embalming their mummies, as appears from the researches of Granville and of Pettigrew, in reference to this curious subject.

When the flesh of animals is subjected to the action of running water, a fatty matter remains, which has been termed *adipocere* (from *adepts* and *cera*); it somewhat resembles spermaceti in appearance, and was supposed to partake of the properties of *fat* and *wax*. In the year 1789, Fourcroy communicated to the Royal Academy of Sciences at Paris, a curious account of the changes sustained by the human bodies interred in the cemetery of the Innocents in that city; some of these had been piled, for a succession of years, closely upon each other, in large cavities containing from one thousand to fifteen hundred individuals. One of these graves, opened in Fourcroy's presence, had been full, and closed for fifteen years. When the coffins were opened, the bodies appeared shrunk and flattened, and the soft solids were converted into a brittle cheesy matter, which softened and felt greasy when rubbed between the fingers. The bones were brittle; and the texture of the abdominal and thoracic viscera no longer discernible, but lumps of fatty matter occupied their places.

It is not uncommon to find masses of this *adipocere* in the refuse of dissecting-rooms, especially when heaps of such offal are thrown into pits and wells, and suffered gradually to decay. The carcasses of cats and dogs, and other drowned animals, also often exhibit more or less of a similar change; and Dr. Gibbes (*Phil. Trans.*, 1794,) found that lean beef, secured in a running stream, underwent a change into fat in the course of three weeks. Fat, and the adipose parts of animals, also undergo a change in appearance and composition under similar circum-



stances: tallow becomes brittle and pulverulent, and may be rubbed between the fingers into a white soapy powder.

Gay-Lussac, Chevreul, and some others, conceive that muscular fibre, skin, &c., is not convertible into adipocere, but that this compound results entirely from the fat originally present in the substance, and that the fibrine is completely destroyed by putrefaction. (See p. 1265.) There are cases, however, in which the conversion of muscle and of fibrine into fat can scarcely be doubted (*Ann. of Phil.*, xii. 41), and it ensues, according to Blondeau, as a consequence of the growth of mycodermic plants; thus in mouldy Roquefort cheese, he traced the conversion of *caseine* into fat to that cause; so also in regard to *fibrine*:—"I took a pound of lean beef slightly salted, and having surrounded it by a layer of paste, placed it in a cellar; in two months it had not putrefied, but was covered with green mould, and converted into a substance resembling hogs'-lard." Blondeau, after describing the parasitic plants which made their appearance, observes, "that they all contain nitrogen, and that their development required ammonia and carbonic acid: the ammonia could only be furnished by the caseine, which in parting with it, passes into *fat*; in fact, the composition of caseine nearly approaches that of fat, if we subtract ammonia." (*Comptes Rendus*, Sept., 1847.)

Connected with the putrefactive changes of organic matter are those extraordinary products of death, and of disease, known under the name of *infectious* and *contagious matters*; their true chemical nature is unknown, except in so far that they appear to possess the general characters of organic compounds, and are decomposed, and resolved into harmless products, by certain chemical agents; amongst which heat, chlorine, and a few of the gaseous acids, are commonly resorted to for the purpose\*. When articles of clothing, or merchandise, which are infected with contagious matter, are exposed for some time to a temperature of about 220°, they become disinfected, especially if at the same time subjected to a current of air. Washing in soap and water, boiling or steaming, are equally effective. In regard to *fumigation*, chlorine is the most effective agent; the mode of applying it, and some of its compounds, in these cases, has already been mentioned. In dissecting-rooms, and in the examination of dead bodies, too much care and attention cannot be paid to the prevention of the evil consequences to which various forms and applications of infectious and contagious products give rise. Their extraordinary power of exciting various and dangerous diseases, either by pulmonary or cuticular absorption, or other introduction into the

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\* In times of plague and other pestilence, the vicinity of smelting-furnaces was formerly resorted to as being least liable to the infectious visitation; the sulphurous and other acid fumes were doubtless the disinfectants. In such and similar situations, in chloride of lime manufactories, and in other chemical works, an immunity from certain diseases is consequently enjoyed, though others are sometimes engendered. It seems not impossible that the freedom which London enjoys from the spread of malignant diseases may, in part,

be ascribed to the products of the combustion of coal, which always taint its atmosphere; the drainage, and the copious supply of water, contribute, however, essentially to the health of its inhabitants, for the effluvia from the offal of large cities, if not speedily and effectively cleared off, is, of course, productive of infinite mischief; even in London, the construction and management of the *sewers* requires much reform, and were it not for the *water-companies*, their evils would be more evident.



living system, are too well known, but of their *modus operandi* we are utterly ignorant: sometimes they produce anomalous and uncertain effects: at others they have a tendency to create poisons in the living system, resembling themselves; the *inoculation* of diseases, as of the small-pox, &c., is a similar case, in which the introduction of the smallest fraction of a grain of poisonous matter excites new and morbid actions, and terminates in the throwing off from the system of a poison corresponding in its properties with that from which it was derived\*. The theory of infection and contagion is mysterious and curious in the extreme, but its further consideration would be foreign to this work. Of another matter also connected with this subject, namely, the influence and production of *malaria*, of *marsh miasma*, and other poisonous exhalations of organic, but principally of *vegetable* origin, we are equally ignorant; they chiefly produce that extraordinary disease, the *ague*, or *intermittent fever*; and their nature is obscure and unintelligible.

### § I. OF THE BLOOD.

IN the higher orders of animals, the blood is of a red color; florid and approaching to scarlet in the arteries, and deep purple in the veins. The specific gravity of the blood varies between 1·049 and 1·057, and its temperature in the healthy human body is between 98° and 100°. According to J. Davy, the normal mean temperature of human blood is 98°·1. (*Phil. Trans.*, 1845, p. 325.) It has an unctuous or somewhat soapy feel, a slightly nauseous odor, and saline taste, and alkaline reaction. It appears homogeneous, or uniform, whilst circulating in its vessels, or immediately upon its removal from them; but when examined by a microscope, it is seen to consist of numerous red spheroidical particles, varying from one-four thousandth to one-six thousandth of an inch in diameter, floating about in a colorless transparent fluid; the former having been termed the *red globules*, the latter the *serous portion*, or *liquor sanguinis*. The accounts given by microscopical observers of the appearance and characters of the globules vary†; they are said to be spherical in mammiferous animals, and elliptical in birds and reptiles. (See in reference to the *blood corpuscles*, BAUER in *Home's Lectures on*

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\* Perhaps one of the most remarkable properties of some forms of infectious matter, is its permanency; retaining, as is frequently the case, its peculiar powers for an indefinite period. Of this, the preservation and transmission of *dried variolous* and *vaccine matter* is a familiar instance. The infection of *scarlet fever* is sometimes retained for weeks and months by articles of wearing-apparel; in one instance, after a malignant form of that disease had prevailed in a house, it was fumigated with chlorine and whitewashed, and every article of furniture and clothing cleansed and fumigated, with the exception of a handkerchief which had been accidentally overlooked, and to which the appearance of the disease, after a period of two months, was probably

attributable. Blankets and woollen goods seem especially retentive of such poisons, and in all doubtful cases should be burned.

† Liebig (*Comptes Rendus*, xii. 539,) found that *globular albumen* might be obtained by diluting serum previously neutralised by an acid. Andral and Gavarret (*Ann. Ch. et Ph.*, Août, 1843,) have rendered it probable that these supposed globules of albumen are the rudiments of an infusorial vegetable; the *Penicillium glaucum*; and that in certain disorders of the mucous membranes, and in purulent discharges, in short, whenever acid albuminous secretions are exposed to air, these filamentous vegetations may make their appearance.



*Comp. Anat.*; YOUNG'S *Medical Literature*; REES and LANE, *Guy's Hospital Reports*, No. 13. MARTIN BARRY, *Phil. Trans.*, 1840, p. 595; and WHARTON JONES, *ibid.*, 1846.)

Under ordinary circumstances, the blood, soon after it has been drawn from its vessels, gelatinizes, or *coagulates*, and the jelly, or coagulum, gradually separates into two parts; a liquid *serum*, and a soft clot or *crassamentum*. In the act of coagulation, the globules apparently coalesce and throw off the coloring matter, which is generally diffused equably through the crassamentum so as to give it an uniform red color; sometimes, however, it subsides, leaving a stratum of colorless coagulum, which, in inflammatory disorders, is called the *buffy coat* of the blood.

It is stated that blood, if rapidly frozen before it has time to coagulate, may be retained for an indefinite time in the frozen state, but that when thawed, it first liquifies, and then coagulates as usual; the coagulation is, at all events, much interfered with by temperature. Blood drawn from a vein in the arm at the temperature of  $53^{\circ}$ , coagulates in 4.5 minutes; at  $98^{\circ}$ , in 2.5 minutes; at  $120^{\circ}$  in 1 minute. Blood which coagulates in 5 minutes at  $60^{\circ}$ , remains fluid for 20 minutes at  $40^{\circ}$ , and requires 60 minutes for complete coagulation at that temperature. (SCUDAMORE *on the Blood*.) When blood is received into a close vessel, its coagulation is somewhat retarded; it is accelerated in the exhausted receiver of the air-pump. When drawn in a full stream, it coagulates more perfectly and more rapidly than when in a very small stream. It appears probable that, in the act of coagulation, the temperature of the blood is very slightly increased, consistently with the laws of latent heat. These are, I believe, the principal facts which have been ascertained upon this subject; they throw no light upon the *cause* of the coagulation\*. The ratio which the clot bears to the serum is variable, and partly dependent upon the shape of the vessel in which the blood is contained: "Two portions of blood were drawn from the same person, one being received and allowed to coagulate in a pear-shaped bottle, and the other in a pint basin; and the ratio of serum to clot was as 1000 to 1292 in the former, and as 1000 to 1717 in the latter. In fact, when a mass of coagulating blood is contained in a spherical vessel, the particles of fibrin, being little removed from a common centre, are more powerfully attracted towards each other, yield a denser clot, and squeeze out more serum than when the coagulation takes place in a shallow wide basin, where the particles are spread over a large surface; the clot of the former is compact and small; while that of the latter being spongy, and hence retaining much serum within it, is large and abundant, though the actual quantity of solid matter is the same in both." (Dr. B. BABINGTON, quoted by Dr. Turner.)

The coagulation of the blood is prevented by all substances which dissolve fibrine, such as caustic potassa or soda; also by excess of their

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\* The cause of the coagulation of the blood is unexplained; it is true that it apparently consists in the aggregation of its globules, but we are ignorant of what it is which prevents this effect in one case and promotes it in another; why the blood remains fluid whilst circulating, and under

other circumstances; and why it occasionally coagulates, *when required so to do*, as in hæmorrhage, to plug up the bleeding vessel, &c. We have no proof that the blood either receives or emits anything essential to its coagulation.

carbonates; and it is more or less retarded or modified by many salts, and by sugar. (See BONNET. *Ann. Ch. et Ph.*, 3ème Sér., xxi. 189.)

The spontaneous coagulation of the blood, and its resolution into serum and coagulum, forms, as it were, a step towards its analysis, and naturally leads to the separate examination of these, its apparent proximate components.

**SERUM OF THE BLOOD.** This is the pale, straw-colored, or greenish-yellow liquid, which gradually oozes out of the cruor or crassamentum; it feels soapy, and has a saline taste, and a specific gravity = 1·027 to 1·030 at 50°. It usually constitutes about three-fourths of the blood, the pressed coagulum forming about one-fourth; it is *alkaline* to tests, slowly reddening turmeric, and rendering the blue of violets green; the readiest test of its alkalinity is litmus paper reddened by acetic acid; to this it immediately restores the blue color. When the serum is heated to about 150°, it becomes a soft solid, coagulating into a translucent mass, which, upon the continuance of heat, becomes more opaque, and gives out a small quantity of a yellowish alkaline liquid, which has been termed *serosity*; this characteristic property is due to the presence of *albumine*, the properties of which have already been detailed, (p. 1219); the serum also contains a small but variable portion of *fat*, and of saline substances.

Marcet and Berzelius have each given an analysis of the serum of human blood; the following are their results. (*Medico-Chirurgical Transactions*, vol. ii.; *Annals of Philosophy*, vol. ii.)

|  | Marcet.       |   | Berzelius.   |
|--|---------------|---|--------------|
| Water .....                                  | 900·0         | Water .....                                       | 905·0        |
| Albumen .....                                | 86·8          | Albumen .....                                     | 80·0         |
| Chlorides of potassium and }<br>sodium ..... | 6·6           | Chlorides of potassium and }<br>sodium .....      | 6·0          |
| Muco-extractive matter .....                 | 4·0           | Lactate of soda, with animal }<br>matter .....    | 4·0          |
| Carbonate of soda .....                      | 1·65          | Soda and phosphate of soda, }<br>with ditto ..... | 4·1          |
| Sulphate of potassa .....                    | 0·35          | Loss .....  | 0·9          |
| Earthy phosphates .....                      | 0·60          |   |              |
|  | <hr/> 1000·00 |   | <hr/> 1000·0 |

Lecanu has also analysed the serum of human blood, and gives the following as its components in 1000 parts. (*Ann. Ch. et Ph.*, xlviii. 317.)

|   | 1 analysis.   | 2 analysis.   |
|---|---------------|---------------|
| Water .....   | 906·00        | 901·00        |
| Albumine .....                                      | 78·00         | 81·20         |
| Organic matters soluble in water and alcohol .....  | 3·79          | 4·60          |
| Fatty matters .....                                 | 2·20          | 3·40          |
| Chlorides of sodium and potassium .....             | 6·00          | 5·32          |
| Carbonate phosphate and sulphate of soda .....      | 2·10          | 2·00          |
| Carbonate and phosphate of lime, magnesia, and iron | 0·91          | 0·87          |
| Loss .....  | 1·00          | 1·61          |
|   | <hr/> 1000·00 | <hr/> 1000·00 |

But it must be observed, in reference to these analyses, that they can only be regarded as averages of the normal composition of the serum: the food and other ingesta greatly affect it, and in disease, abnormal substances are found in it. The proportion of fatty matter is especially



liable to vary, and bile, sugar, urea, coloring-matter, peculiar salts, and other substances may be detected in it in certain diseases, and under certain courses of medicine. In cases of *milky serum*, the quantity of fatty matters amounts sometimes to as much as from 10 to 11·7 per cent. (ZANARELLI. LECANU. DUMAS.)

CRASSAMENTUM. COAGULUM. These terms are applied to that part of the blood which spontaneously coagulates, and then gradually contracts into a more or less dense mass. When cautiously removed from the serum in which it is immersed, and of which it always retains a considerable proportion, it may be regarded as principally consisting of *fibrine* and *coloring matter*.

*Fibrine* may be separated from the serum and coloring matter, by washing it in repeated portions of cold water; or by stirring recently-drawn blood with a stick, to which the coagulum will adhere, and it may then be conveniently washed in running water, till the serum and color are extracted, and the fibrine remains in the form of a nearly colorless and fibrous substance, insoluble in cold water. Berzelius obtains fibrine by cutting the clot of blood into thin slices, drying them upon folds of blotting paper to absorb the serum, and then washing with water till all soluble matters are extracted. The fibrine, however, still retains a little fat, for the removal of which it must be digested in ether, or in warm anhydrous alcohol.

The colorless layer occasionally observed upon blood drawn in inflammatory diseases, and termed the *buffy coat*, when washed, digested in ether, and dried, has been considered as nearly pure fibrine, and identical with the part of blood termed *coagulable lymph*. According to Mulder, the buffy coat is an *oxide of proteine*, or a combination of fibrine and oxygen. (*Chem. Gaz.*, March, 1844.)

The distinctive chemical properties of *fibrine* have been described above (p. 1227).

COLORING MATTER OF THE BLOOD. HÆMATOSYNE. HÆMACHROME. It is doubtful whether the coloring matter of the blood can be effectually separated from other principles, especially from albumine. Vauquelin advises the digestion of the coagulum, drained of serum, in dilute sulphuric acid at a temperature of 160°. The liquid, filtered while hot, is to be evaporated to half its bulk, and nearly saturated with ammonia; the coloring matter falls, and is to be washed and dried. (*Ann. Ch. et Ph.*, i.) But in this process the hæmatosyne has probably undergone change.

Dr. Rees has rendered it probable that the coloring globules of the blood are vesicles containing a red fluid, the coats of which are susceptible of endosmose and exosmose; that when immersed in saline solutions denser than their included fluid, they collapse, owing to exosmose; in lighter fluid, as in water, they are distended and ruptured by endosmose; in fluid of the same density as their included liquor, they remain unaltered: and upon this view he explains certain phænomena of disease. (*Guy's Hosp. Rep.*) He suggests, therefore, as the best mode of obtaining the coloring portion of the globules, to wash the clot in the serum, from which, after some hours, the globules subside; the supernatant serum is then decanted and drained from the globules, which are put into distilled water, by which they are burst, and their coloring liquid

taken up by the water, whilst the including membranes, and their nuclei, are deposited as a colorless sediment. On evaporating the clear colored solution, and incinerating the residue, the whole of the iron was found in it, and none in the colorless deposit.

The chemical properties of the coloring matter of the blood seem to show that it is a peculiar animal principle. It is soluble in cold water, and the solution, when boiled, deposits a brown sediment of altered coloring matter. Hydrochloric, dilute sulphuric, and several of the vegetable acids, and the caustic and carbonated alkalis, readily dissolve it, and form solutions of different tints of red, and of a peculiar greenish hue when viewed by transmitted light. Nitric acid instantly renders these solutions brown, and decomposes the red principle. These and other properties (*Phil. Trans.*, 1812), led me to regard the coloring matter of the blood as a *distinct proximate principle*, independent of the presence of iron, to which metal its peculiarities were at one time referred by Fourcroy and Vauquelin; and the latter chemist verified this conclusion in the above-quoted memoir.

According to Berzelius, the crassamentum of the blood consists of

|                           |       |
|---------------------------|-------|
| Coloring matter .....     | 64    |
| Fibrine and albumine..... | 36    |
|                           | <hr/> |
|                           | 100   |

and the coloring matter, when incinerated, affords a residue consisting of

|                                       |       |
|---------------------------------------|-------|
| Oxide of iron .....                   | 50·0  |
| Subphosphate of iron .....            | 7·5   |
| Phosphate of lime with magnesia ..... | 6·0   |
| Lime .....                            | 20·0  |
| Carbonic acid and loss .....          | 16·5  |
|                                       | <hr/> |
|                                       | 100·0 |

The iron he regards as contributing to the red color of the blood, and a hint has been thrown out by Dr. Ure, as to the possibility of its being derived from sulphocyanide of iron.

Berzelius examined the solution of the coloring matter obtained by washing the coagulum, deprived of its serum, in water. The strong filtered aqueous solution, thus obtained, is dark brownish-red, and becomes brighter by dilution; evaporated at 100°, it leaves a dark residue, soluble in water; but a boiling heat changes, and renders it insoluble. Chlorine darkens the concentrated solution, and then gradually destroys its color; alcohol coagulates, and renders it insoluble: the acids generally decompose it. Acetic acid heightens the color of the solution of hæmatosyne, but does not precipitate it: on neutralizing the acetic acid by potassa, the hæmatosyne is precipitated. Weak alkaline solutions act nearly similarly. Sulphuretted hydrogen renders the solution of hæmatosyne first violet, then green, and the red color is not restored either by alkali or acid. Hæmatosyne is thrown down of a *red* color by acetate of lead, sulphate of zinc, and corrosive sublimate; and *brown* by nitrate of lead, of silver, and of copper, and by chloride of gold, and of platinum.

Among the latest experiments on the blood-globules are those of Figuier (*Ann. Ch. et Ph.*, August, 1844); he separates the fibrine by stirring, and then adds solution of sulphate of soda, which prevents the



globules passing through a filter, upon which they may be collected; the filtered liquor contains the albumine and salts; the former may be obtained by coagulation. By this mode of analysis the blood he examined yielded water 802·9; globules 130·6; fibrine 3·9; albumine 50·6; salts 12·0. From the globules collected as above, the coloring principle may be obtained by digesting them in ammoniacal alcohol; the solution is evaporated, and the residue, heated with ether to separate a little fat, is *hæmatosyne*. Figuier considers the globules as made up of *hæmatosyne*, albumine, and fibrine.

The experiments of Stevens and of Squire, have also illustrated the peculiar nature of *hæmatosyne*. One of its most striking characters is the change of tint which it apparently suffers by the action of air, and which is well seen in the exposure of venous blood to the contact of air, or of oxygen. The coloring matter of the blood is also rendered florid and brilliant, even when in its blackest and venous state, by almost all neutral salts; with sulphate of soda, for instance, or with nitrate of potassa, the effect is extremely striking. Acids and alkalis generally render the *hæmatosyne* black; tartaric, citric, and even carbonic acid produce this effect; they exert more or less solvent power over it, and their solutions are dingy, and often nearly black, by reflected light, but of a peculiar green tint by transmitted light; the intensities of these colors depending upon their states of dilution. Acid salts, and basic salts, act more or less as free acids or alkalis. In neutrosaline solutions, on the other hand, *hæmatosyne* is insoluble; and if its dark colored acid, and alkaline solutions, be so mixed as accurately to neutralize each other, the *hæmatosyne* falls, and acquires a florid tint. To observe the action of acids, alkalis, and salts, upon *hæmatosyne*, to the utmost advantage, the blood should not be suffered to coagulate, but received, whilst flowing, into the acid, alkaline, or saline solution. These facts have been applied by Dr. Stevens to explain the changes of color which blood suffers in passing from the venous to the arterial state. (*London Medical Gazette*, April, 1834.) He shows, that *venous blood* contains carbonic acid, and that it gives it off when drawn from the arm into a vessel filled with hydrogen, all contact with air or oxygen being carefully avoided, so as to preclude the formation of carbonic acid by the union of carbon in the blood with the oxygen of the air: that this carbonic acid blackens the *hæmatosyne*, and that its red color is restored by its removal, when the saline matters of the blood render it florid: that the change of arterial to venous, or of florid to black blood, occurs in the extreme ramifications of the vessels, or in their capillary anastomoses, for the blood is arterial in the extreme arteries, and venous in the extreme veins: Dr. Stevens also infers that *arterial blood* contains atmospheric air, or air more abundant in oxygen than that of the atmosphere; and that the removal of the carbonic acid in the lungs is effected by a peculiar attractive power of oxygen for carbonic acid, taking place through the membrane of the lungs; he concludes, and adduces satisfactory experiments in proof of the conclusion, that the change of venous into arterial blood, is not the result of the absorption or combination of oxygen, but of the loss or abstraction of carbonic acid by or from the black blood; the *blackening* cause being thus removed, the saline matter present becomes efficient as the *reddening* cause; for Dr. Stevens has proved that if the salts be abstracted from the

coloring matter, it retains its black color, notwithstanding the loss of carbonic acid; and that a piece of highly-florid coagulum becomes black when its salts are washed out, and can only again be rendered florid by the addition of saline matter\*. These facts have important bearings upon the theory of respiration, but the presence of carbonic acid in arterial as well as in venous blood (MAGNUS, *Ann. Ch. et Ph.*, LXV. 169; GAY-LUSSAC, *Ann. Ch. et Ph.*, Mai, 1844,) shows that its evolution in the lungs cannot be the sole or even the principal cause of the change of color.

It will appear from the preceding statements that there is much contradictory evidence in the chemical history of the blood globules, and that all that can certainly be said respecting them is, that they contain iron, a peculiar coloring principle, and a proteine compound very analogous to albumine; some chemists have assigned to the latter, the distinctive name of *globuline*.

Liebig observes that the leading characteristic of the red globules is that they contain a compound of iron found in no other constituent of the body, and that they have the power of combining with gases, as evidenced by the change of properties which they suffer when exposed to their action; their change of color being sometimes referrible to decomposition, and sometimes to combination: that when darkened by carbonic acid they again become florid in oxygen, and therefore that the compound which they form with carbonic acid is decomposed by oxygen. He then proceeds to argue that the iron compound in the globules has the characters of an oxidized compound, being decomposed by sulphuretted hydrogen precisely in the same way as the oxides of iron; and that the compounds of protoxide of iron have the property of depriving other oxidized compounds of oxygen, while the compounds of peroxide of iron give up oxygen with comparative facility. On these, and other grounds, he is of opinion, that in arterial blood the iron of the globules is in the state of *peroxide*, whilst in venous blood it is in the state of *protocarbonate*.

To the statement now given of the nature and properties of the components of the blood, the following facts respecting the *odor* of different kinds of blood have been added by M. Baruel. Whilst preparing the coloring matter of blood according to Vauquelin's process, the clot of ox-blood was heated with excess of sulphuric acid of moderate strength, on which occasion a strong odor of beef was observed. Some time after, having occasion to operate upon the blood of a man

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\* Dr. Stevens observes that there is an apparent exception to the blackening effect of acids on the blood. "As the carbonates are weaker salts than those that are formed with fixed acids, and as the alkaline carbonates form a considerable portion of the natural saline matter of the blood, it follows that when we add an acid solution that is just strong enough to convert this weaker into a stronger salt, we then brighten the color. It is for this reason that a salt with a slight excess of acid increases the arterial appearance. It is also for the same reason that there is generally an increased glow of red when we first mix any of the

acids with the warm blood; but if we add a very small proportion more of a fixed acid than is just sufficient to convert the alkaline carbonates into neutral salts, the red color is so irretrievably destroyed by the excess of acid, that with the addition of a little water, the whole is converted into a fluid which exactly resembles the black vomit." (*Observations on the Blood*, by WILLIAM STEVENS, M.D.; London, 1832.) See also a paper by Magnus, (*Poggend.*, XL. 583,) in which the presence of carbonic acid, oxygen, and nitrogen, is shown both in venous and in arterial blood.



who had taken opium, the fluid was first coagulated by heat, and divided, after which it was boiled with weak sulphuric acid: immediately so strong an odor of the sweat of man was evolved, as to infect the whole laboratory, and render it necessary for the persons to leave the place. This and the former fact combined, induced M. Baruel to extend his experiments on these subjects, and the following are the results he obtained.

i. The blood of each species of animal contains a principle peculiar to each. ii. This principle, which is very volatile, has an odor resembling that of the sweat, or the cutaneous or pulmonary exhalation of the animal from which the blood was taken. iii. In the blood, this volatile principle is in a state of combination, its odor being then insensible. iv. When the combination is broken, this principle is volatilized, when it is easy to recognise the animal to which it belongs. v. In each species of animal, this principle is more decided, or has more intensity of odor in the male than in the female; and in men, the color of the hair accompanies certain variations in this principle. vi. This principle is in a soluble state in the blood, and may be found, therefore, either in the unaltered blood, or after the fibrine has been removed, or even in the serosity of blood. vii. Of all the means of separating this principle, concentrated sulphuric acid has succeeded best.

To obtain these results, it is only necessary to put a few drops of blood, or the serum of blood, into a glass, to add concentrated sulphuric acid to the amount of one-third or half as much as of blood, and to stir the whole together; the odoriferous principle is immediately rendered evident. By these means, M. Baruel can readily distinguish the blood from the following sources. i. That of a man disengages a strong odor of the perspiration of man, which it is impossible to confound with any other. ii. That of a woman, a similar odor, much weaker, and resembling the perspiration of woman. iii. That of the ox, a strong odor of beef. iv. That of the horse, a strong odor of the perspiration of the horse. v. That of the sheep, a strong odor of wool impregnated with the perspiration of that animal. vi. That of the dog, the odor of the transpiration of a dog. vii. That of a pig, the disagreeable odor of a piggery. viii. That of a rat, the bad odor belonging to the rat. The same result has been obtained with the blood of various kinds of birds, and even with the blood of a frog, which gave the strong odor of marshy reeds, &c., and with that of a carp, which gave a principle smelling like the mucus which covers the bodies of fresh-water fish.

Upon trials made to ascertain whether spots of blood could be distinguished, and referred to their source, M. Baruel found, that to a certain extent, a pretty sure judgment could be given, even after fifteen days or more. The spotted linen is to be cut out, put into a watch-glass, and being moistened with a little water, is to be left for a short time at rest. When well moistened, a little concentrated sulphuric acid is to be added, and stirred about with a glass rod; then, by respiring near it, the odor may be perceived. M. Baruel is not sure that the distinction could be ascertained after more than fifteen days, and therefore recommends legal officers to allow of no delay in any experiments, which bear upon cases of judicial investigation. According to Couerbe and Soubeiran, Baruel's tests are useful, but not so decisive as he represents them. (DUMAS. *Chim. app. aux Arts*, viii. 478.)

A question has sometimes arisen as to the possibility of preserving blood, with its principal characters either unimpaired or little altered; the following facts will, perhaps, illustrate this point. In the month of May 1818, blood was drawn from the arm into six phials, each holding about two ounces; these were secured by good corks, which were cemented over, and put away in a closet, where they remained till May 1833, a period of 15 years. Two of the phials were then opened. The blood was perfectly liquid without any appearance of coagulum; there seemed to have been no extraordinary evolution of gaseous matter, but it exhaled a nauseous and slightly-putrid odor, with a trace of sulphuretted hydrogen. It was of a dark-purple color, but became florid-red and was coagulated upon the addition of a few drops of solution of corrosive sublimate; it was blackened and coagulated by acids; alcohol also coagulated it: and the action of acetic acid and of ferrocyanide of potassium, resembled that upon fresh serum. The chief apparent change, was loss of power of spontaneous coagulation. Heat, and electricity, coagulated it. On opening another of these phials in January 1848, the blood was found precisely in the same condition.

Having enumerated the principal facts which bear upon the chemistry of the blood, I shall now subjoin the results of its analysis by Lecanu (*Ann. Ch. et Ph.*, LXvii. 54), to whom we are indebted for much curious information and laborious research in this difficult subject. He considers the venous blood of man, in its normal state, as composed of

|                |       |
|----------------|-------|
| Serum .....    | 869   |
| Globules ..... | 131   |
|                | <hr/> |
|                | 1000  |

or of

|                                     |          |           |
|-------------------------------------|----------|-----------|
| Water .....                         | 790·3707 |           |
| Oxygen .....                        | }        | 10·980    |
| Nitrogen.....                       |          |           |
| Carbonic acid .....                 |          |           |
| Extractive matters .....            |          |           |
| Phosphorized fat .....              |          |           |
| Cholesterine .....                  |          |           |
| Serotine .....                      |          |           |
| Free oleic acid .....               |          |           |
| Free margaric acid .....            |          |           |
| Chloride of sodium.....             |          |           |
| Chloride of potassium .....         |          |           |
| Chloride of ammonium .....          |          |           |
| Carbonate of soda .....             |          |           |
| Carbonate of lime .....             |          |           |
| Carbonate of magnesia .....         |          |           |
| Phosphate of soda .....             |          |           |
| Phosphate of lime .....             |          |           |
| Phosphate of magnesia .....         |          |           |
| Sulphate of potassa .....           |          |           |
| Lactate of soda .....               | }        | 67·8040   |
| Salts of fixed fatty acids .....    |          |           |
| Salts of volatile fatty acids ..... |          |           |
| Yellow coloring matter .....        |          |           |
| Albumine of the serum .....         |          | 130·8453  |
| Globules .....                      |          | <hr/>     |
|                                     |          | 1000·0000 |



He considers the globules as constituted of

|                  |          |
|------------------|----------|
| Fibrine .....    | 2·9480   |
| Hæmatosine ..... | 2·2700   |
| Albumine .....   | 125·6273 |
|                  | <hr/>    |
|                  | 130·8453 |

The fluctuations in the composition of healthy blood he represents as follows:—

| For the water.                                       | For the saline<br>extractive and<br>fatty matters. | For the albumine<br>of the serum.                  | For the globules.                                    |
|--|--|--|--|
| $\overbrace{\text{from } 805\cdot263}$<br>to 778·625 | $\overbrace{\text{from } 14\cdot060}$<br>to 8·870  | $\overbrace{\text{from } 78\cdot120}$<br>to 57·890 | $\overbrace{\text{from } 148\cdot450}$<br>to 115·850 |

Lecanu has also given the following statement of the comparative analysis of blood drawn from ten men and ten women.

|                                   | Males.  |       | Females. |
|-----------------------------------|---------|-------|----------|
| Water.....                        | 789·32  | ..... | 804·37   |
| Albumine .....                    | 67·50   | ..... | 69 72    |
| Saline and extractive matter..... | 10·69   | ..... | 9·95     |
| Red globules .....                | 132·49  | ..... | 115·96   |
|                                   | <hr/>   |       | <hr/>    |
|                                   | 1000·00 |       | 1000·00  |

According to Lecanu the proportion of the red globules may be regarded as a measure of the vital energy, for the action of the serum and of the globules upon the nervous system is very different; the former scarcely excite it, while the latter do so powerfully: it would also appear that every cause which tends to diminish the mass of blood tends at the same time to a diminution of the relative proportion of the globules; hence the effect of bleeding, uterine evacuations, &c.

In reference to the difference between arterial and venous blood, Lecanu concludes that the color and odor of the former are more intense, that it has more tendency to coagulate, and contains more globules, less water, and more free oxygen in proportion to its carbonic acid.

Comparative experiments have been made on the blood of different animals by Prevost and Dumas, by Tiedemann and Gmelin, and by other physiologists and chemists, for the details of which I must refer to their respective works: the general results are, that the globules vary in size and form, and that the components differ somewhat in their relative proportions, rather than in their essential qualities. In all animals the relative proportion of the aqueous to the solid part of the blood is liable to fluctuation, even in the healthy state, hence discrepancies in its specific gravity; it is probable also that the quantitative if not the qualitative composition of the blood varies in different vessels and different parts of the body; hence, perhaps, the slight difference observed in blood abstracted by cupping, as compared with that drawn from the arm; hence too, there is a difference in the blood drawn from a vein in the arm, and that from a vein returning from some large gland, such as the kidney or liver. (See also in reference to this subject, "*Recherches sur la Composition du Sang de quelques Animaux Domestiques dans l'état de Santé et de Maladie, Par MM. Andral Gavarret et Delafond.*" *Ann. Ch. et Ph.*, 3ème Sér., v. 304.) Henneberg found silicate of soda in the

blood of fowls, and hence explains the origin of the silica said to be found in feathers. (*Chem. Gaz.*, Feb. 1847.)

**BLOOD IN DISEASE.** We are but imperfectly acquainted with the changes in the composition of the blood which are the result of disease. The morbid changes of the blood resolve themselves into those dependent upon excess or deficiency of its usual components, and those in which foreign substances are detected in it; but the composition of the blood is such as to interfere in almost all cases with the nice indications of delicate tests, and the quantity of foreign matters which render the blood diseased in some cases are so small, as to elude very accurate observation.

In cases in which the functions of the kidneys are much disturbed, urea is detected in the blood; and where the secretion of the urine is suspended, it is present in considerable quantity, and the source probably of the fatal consequences that ensue from that cause. Prevost and Dumas tied the renal vessels, and extracted the kidneys of a dog, and on the second day after the operation, they obtained no less than 20 grains of urea from 5 ounces of his blood. (*Ann. Ch. et Ph.*, xxxiii. 90.) Urea has also been detected by Dr. O'Shaughnessy in the blood of patients suffering under cholera, in which disease the renal functions are usually much disturbed\*. In jaundice, the coloring principles of the bile occasionally exist in the blood, and are discernible in the serum. It not unfrequently happens that the serum of the blood resembles whey, or milk and water; and sometimes it resembles cream; but such cases are very rare; these appearances depend upon the presence of fatty or oleaginous matter, which may be separated by agitation with ether. Drs. Traill and Christison procured 1 *per cent.* of fat from opalescent serum, and as much as 5 *per cent.* from serum which had the appearance of milk. (*Edinb. Med. and Surg. Journ.*, April, 1830.) In some nervous fevers of a typhoid character, the blood is said, during the increase of the disorder, to be more aqueous or thin than in health, and gradually to become more dense during its decrease. The state of the blood in cholera has excited a good deal of attention. The peculiar whitish or whey-like discharge from the bowels, is said to contain albumine, and the salts of the blood, with particles of fibrine; the density of the blood

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\* Dr. Rees has ascertained that there is no trace of urea in the serum of healthy blood: but in certain cases of disease he has found it in proportions varying from 0.5 to 0.2096 in the thousand parts: he recommends the following process for the separation of urea: "The serum, or effused fluid, is evaporated at a heat somewhat below 212° Fahrenheit; the dry mass is broken up; boiling water thrown upon it, and allowed to digest several hours. This liquor being poured off, a second portion of water is added, and allowed to digest; after which, the whole is thrown on a filter, and the solid matters washed with distilled water till the percolating fluid ceases to affect a solution of nitrate of silver. The filtered liquors are next evaporated to dryness, by a gentle heat; and the extract digested in a stopper-

bottle, with ether of the sp. gr. 0.754. This menstruum extracts the urea only; and by digesting successive portions of it until the last added yields no deposit of that principle on evaporation, we obtain the whole of the urea present, and thus directly estimate its weight. As obtained by this process, urea is pure and colorless. It once happened to me to observe some slight contamination of the urea, obtained as above, by fatty matter which had escaped separation with the albumen: this, however, was easily got rid of, by dissolving the urea in distilled water, and throwing the solution on a filter previously moistened, when the fatty matter remained behind, and allowed the urea to pass through, perfectly pure."—(*Guy's Hospital Reports*, No. X.)



itself is above the natural standard, it is of a remarkably dark color throughout the system, and sometimes viscid, and incapable of coagulation, but at the same time deficient in saline matter. These appearances have been ascribed to various causes. According to Dr. Thomson, the blood in cholera is wholly unsusceptible of the usual influence of the air, and is consequently decidedly altered in its nature. Dr. O'Shaughnessy however found, that it did become florid when agitated with air, and that it emitted carbonic acid gas. Dr. Stevens ascribes the appearances to deficiency in saline matter, and successfully treated such cases, not only by the administration of solutions of common salt and of chlorate of potassa, but by the actual injection of solution of salt into the veins. Dr. Turner observes, that the most correct opinion perhaps is, that the blood of persons in cholera, in consequence of deranged arterial action, circulates sluggishly, and is therefore imperfectly arterialized, and that the dark color may arise from that cause, independent of any diminution of saline matter, and may disappear, from an improved circulation, without the administration of salt; although there is no doubt that loss of saline matter increases the dark tint of the blood, and prevents it from acquiring the arterial color. The secretion of a large quantity of saline fluid by the intestines in these cases, the decided deficiency of salts in the blood, and the relief afforded by restoring saline matter to the system, are, however, strong points in favor of Dr. Stevens's views. The substance ejected from the stomach in the last stage of yellow fever, and known under the name of *black vomit*, is blood blackened and coagulated by the free acid of the stomach.

Messrs. Andral and Gavarret, in an elaborate paper on the influence of disease on the composition of the blood (*Ann. Ch. et Ph.*, LXXV. 225), have arrived, among other interesting conclusions, at the following:—1. That in acute inflammations (phlegmasiæ) the fibrine of the blood is in excess, and that there is a disposition to its rapid formation. 2. That in febrile diseases (pyrexia), where any modification of the blood is perceptible, the relative proportion of the globules to the fibrine sustains an increase. 3. That in certain cachexiæ, and diseases of debility, there is a deficiency in the globules. 4. That in cases of albuminous urine the albumine of the blood sustains an equivalent diminution. (See also upon this subject the researches of Becquerel and Rodier, and of Simon, a copious abstract of which is given by Dumas. *Chim. App. aux Arts*, viii. 500, &c.)

**DETECTION OF BLOOD.** It is occasionally important in juridical inquiries, to distinguish between stains upon metal and linen arising from blood, and those from other sources. Orfila has given some useful information upon this matter, and an abstract of the whole subject will be found in Taylor's *Manual of Medical Jurisprudence*, p. 332. Ed. 1844.

*Blood-stains on Steel.* When the blade of a knife is stained by blood, it is *red* when the layer is very thin, but *brown* if thicker: heated to about 80°, the blood-spot peels off, leaving the steel tolerably clean; no such appearance arises from common rust, but something like it may be produced by the juice of fruits; in that case the blood spot may be distinguished from that of vegetable juices, by collecting the portion

which scales off, and heating it in a bit of glass tube closed at one end; it exhales the odor of animal matter and ammonia, and the latter may be recognised by its *alkaline* reaction on test-paper: any of the vegetable stains would, under such circumstances, exhale *acid* fumes; and mere rust would either give out nothing, or at all events, the slightest possible trace of ammonia. Where it is practicable, the following process is more exact; the stained steel is immersed in water; the hæmatosyne and some albumine gradually dissolve, and leave the fibrine on the blade, from which it may be removed by the nail; red streaks form in the water, which becomes red at bottom: divide this red part into several portions; to 1 add chlorine; it becomes green, then colorless, and then deposits white flakes. To 2 add ammonia, which does not alter the color, when from blood, but if from any ordinary dye-stuff, it becomes purple. Into 3 drop nitric acid; it becomes pale-gray. Into 4 a drop or two of infusion of galls; it does not alter the color, but occasions a slight cloud. Heat 5 till it boils, when it either deposits flakes, or becomes opalescent. Of these tests, nitric acid and infusion of galls are the most delicate; should rust of iron have mingled itself with the liquid, it may be separated by filtration.

*Blood-stains on Linen, &c.* Suspend the piece of linen in a little water; the fibrine remains upon it, and may be detected by the evolution of ammonia, if linen or cotton, on the application of a sufficient degree of heat, in a small tube; but the hæmatosyne and some albumine are dissolved or extracted; test the colored solution as above directed. Should the blood have coagulated upon one piece of linen, and then have gone through, so as to discolor another, no fibrine will be found on the latter. It is possible that a solution of madder, or some such coloring matter, in a serous or albuminous liquid, might lead to deception; but in this case the stain upon the linen would not be so easily removed by water, and the red solution would become yellow by acids, and violet by alkalis; a mixture of serum and the red of madder is rendered yellow, and does not remain red, on adding infusion of galls.

## § II. MILK.

THIS fluid, secreted by females of the class *mammalia* for the nourishment of their young, is a white, translucent, aqueous emulsion, the principal components of which are the oily compound called *butter*, *curd*, or *caseine*, a species of *sugar*, and certain salts.

Under the microscope the milk appears as a transparent fluid, in which small white globules are diffused, of variable diameters in the same milk, as well as in that of different animals; the globules of human milk being generally larger than those of cow's milk. These globules collect upon the surface of the milk, when it is left at rest, forming *cream*. They are by some stated to be mere naked globules of fatty matter; by others they are regarded as having a distinct containing membrane; and this is most probable, inasmuch as they do not coalesce by standing, or when gently heated, nor does ether directly dissolve them: but when acetic acid is added to milk, it appears to dissolve the containing caseous or albuminous membrane, and the globules then coalesce into greasy drops which ether readily takes up.



It is generally stated that milk always presents a slight acid reaction, referred by Berzelius and others to the presence of free *lactic acid*; it is however probable that perfectly fresh milk is entirely free from acid. According to D’Arcet and Petit, cow’s milk is sometimes alkaline and sometimes acid; alkaline when pastured, but acid when stalled. They also state that woman’s milk is always alkaline, and that it retains its alkalinity for some time, if from healthy individuals; but soon acidifies when taken from delicate or sickly persons. The milk of all animals is said to be easily rendered alkaline by alkaline food; but in its normal state it seems to be very nearly neutral, though it soon exhibits acidity when exposed to air, in consequence of the formation of lactic acid.

The sp. gr. of milk varies; that of the cow is generally about 1·030. It fluctuates in different animals, according to Brisson, from 1·0203 to 1·0409 (*Pesanteur Specifique des Corps*, Paris, 1787, p. 389), but as it is affected by the presence of the butter on the one hand, which diminishes, and by the caseum and salts on the other, which increase its density, it is difficult to estimate a mean.

Some of the leading properties of milk are to be ascribed to the presence of *caseine*, a form of *proteine*, the chemical peculiarities of which have already been described (p. 1231). Its other ingredients, namely, *butter*, and *sugar of milk*, and the changes which the latter suffers in the formation of lactic acid, remain to be noticed.

According to Berzelius the sp. gr. of skimmed milk is 1·033; that of cream 1·024; and they consist of

| Skimmed Milk.  |        |  | Cream.       |       |
|--|--------|--|--------------|-------|
| Water .....  | 928·75 |  | Butter ..... | 4·5   |
| Caseous matter or curd, with a trace of butter                             | 28·00  |  | Curd .....   | 3·5   |
| Sugar of milk .....  | 35 00  |  | Whey .....   | 92·0  |
| Hydrochlorate and phosphate of potassa .....                               | 1·95   |  |              |       |
| Lactic acid, acetate of potassa, and a trace of }<br>lactate of iron ..... | 6·00   |  |              | 100·0 |
| Earthy phosphates .....  | 0·30   |  |              |       |
|  | 100·00 |  |              |       |

Haidlen obtained the following results from 100 parts of cow’s milk, and woman’s milk. (*Ann. der Pharm.*, XLV. 263.)

| Cow’s Milk.                           |      |     | Human Milk. |     |     |
|---------------------------------------|------|-----|-------------|-----|-----|
| Butter .....                          | 3·0  | ... | 3·4         | ... | 1·3 |
| Sugar of milk and soluble salts ..... | 4·6  | ... | 4·3         | ... | 3·2 |
| Caseine and insoluble salts .....     | 5·1  | ... | 3·1         | ... | 2·7 |
|                                       | 12·7 |     | 10·8        |     | 7·2 |

From 100 parts of the milk of two cows, he obtained the following salts.

|                             |       |     |       |
|-----------------------------|-------|-----|-------|
| Phosphate of lime .....     | 0·231 | ... | 0·344 |
| Phosphate of magnesia ..... | 0·042 | ... | 0·064 |
| Phosphate of iron .....     | 0·007 | ... | 0·007 |
| Chloride of potassium ..... | 0·144 | ... | 0·183 |
| Chloride of sodium.....     | 0·024 | ... | 0·034 |
| Soda .....                  | 0·042 | ... | 0·045 |
|                             | 0·490 |     | 0·677 |

The statements respecting the composition of human milk are much at variance, arising probably in part from the difficulty of obtaining it in sufficient quantity for analysis, and partly from its mutability in regard to the relative proportions of its component parts. L. Gmelin (*Handbuch*), and Berzelius (*Lehrbuch*), have each given the details of the experiments which have been made upon it. Its specific gravity appears to vary between 1·020 and 1·025, or a little higher: its solid contents, according to Meggenhofer, vary between 11 and 12·5 *per cent.*, and its caseine is said to furnish soluble combinations with acids, so that it is not coagulated by them. Of fifteen samples, only three were coagulated by acetic and hydrochloric acids; but they were all coagulated by *rennet*: this seems to establish the distinct action of rennet from that of acids. The following are the results of three of Meggenhofer's analyses:—

|                                | I.    | II.   | III.  |
|--------------------------------|-------|-------|-------|
| Butter, acids, and salts ..... | 9·13  | 8·81  | 17·12 |
| Sugar of milk and salts .....  | 1·14  | 1·29  | 0·88  |
| Curd coagulated by rennet .... | 2·41  | 1·47  | 2·88  |
| Water .....                    | 87·25 | 88·35 | 78·93 |

The extraordinary proportion of butyraceous matter in III. shows the uncertainty of composition in this secretion: indeed, in all the above cases, the quantity of butter appears to have been excessive. Payen's results, which in regard to the total amount of solid matter, agree with Meggenhofer's, do not give an average of more than 5·2 *per cent.* of that ingredient; and Haidlen's still less.

Numerous analyses of milk have been published, besides those above quoted, the results of which have been tabulated by Dumas, (*Ch. App. aux Arts*, viii. 655,) who has also given the results of experiments upon the influence of food upon the composition of milk. He finds that where animals are fed upon vegetables, or upon a mixture of animal and vegetable food, the milk always contains albuminoid matter, represented by caseum, fatty matters represented by butter, saccharine matter represented by sugar of milk, and divers salts. In *carnivora*, the sugar always seems wanting. Thus the milk of a bitch fed for 15 days upon horseflesh, contained,

|                                   |       |
|-----------------------------------|-------|
| Water .....                       | 74·74 |
| Butter .....                      | 5·15  |
| Extractive matter and salts ..... | 4·13  |
| Caseine and salts .....           | 15·85 |

The same bitch, fed for 15 days upon bread soaked in greasy broth, yielded milk composed of

|  |       |
|--|-------|
| Water .....                                      | 81·10 |
| Butter .....                                     | 3·09  |
| Extractive matters, sugar of milk and salts .... | 4·40  |
| Caseine .....                                    | 11·39 |

and after the further continuance of the same diet for 15 days more, the milk of the same animal yielded

|  |       |
|--|-------|
| Water .....                                      | 75·0  |
| Butter .....                                     | 6·84  |
| Extractive matters, sugar of milk and salts .... | 5·04  |
| Caseine .....                                    | 12·17 |



In these cases the sugar of milk was obtained in crystals, and analyzed, so as to leave no doubt of its nature; but in no case where the animal was exclusively fed upon animal food, could sugar be detected.

We also have an analysis of the milk of a carnivorous bitch, by Simon, who found it composed of

|                         |       |      |       |
|-------------------------|-------|------|-------|
| Caseine .....           | 17·40 | .... | 14·60 |
| Butter.....             | 16·20 | .... | 13·30 |
| Extractive matter ..... | 2·90  | .... | 3·00  |
| Salts .....             | 1·50  | .... | 1·48  |
| Water .....             | 65·74 | .... | 68·20 |

Many experiments have been made by Peligot (*Ann. Ch. et Ph.*, LXXII. 431), by Boussingault (*ibid.*, LXXI. 65; 3ème Sér., xii. 185), by Playfair (*Mem. Chem. Soc.*, i. 174), and others, illustrating the effects of food upon the quantity and quality of milk, the details of which would occupy more space than I can here assign to them: the general results are given by Dumas, (*Chim. app. aux Arts*), and by Johnstone (*Lectures on Agricult. Chem.*, 786.)

*Asses' Milk* has a specific gravity = 1·023 to 1·0355; it yields a light white butter, which soon grows rancid: the curd is more difficultly separable than from cows' milk, but the whey is clearer, and contains more sugar of milk. It contains 2·9 cream, 2·3 caseum, 4·5 sugar of milk (*per cent.*): and, according to Luisius and Bondt, it is susceptible of vinous fermentation.

*Mares' Milk* has a specific gravity = 1·034 to 1·045: it yields little cream, but a large proportion of sugar of milk; a vinous liquor is obtained by the fermentation of its whey, known in Tartary under the name of *koumiss*.

*Goats' Milk* is of a specific gravity = 1·036; its goaty odor is stronger from dark than from white goats; it yields much cream and butter, and this, besides the usual acids, yields a peculiar one, called by Chevreul *hircic acid*, which gives it its characteristic odor: its caseum is also abundant, and the whey easily pressed out of it. It contains in the 100 parts, 4·08 butter, 4·52 caseum, 5·86 residue of the whey, 85·50 water (PAYEN.) 7·5 cream, 4·56 butter, 9·12 caseum, 4·38 sugar of milk. (S. LUISIUS and BONDT.)

*Sheep's Milk*, of the specific gravity of 1·035 to 1·041, yields much cream, the butter of which is semifluid, and easily becomes rancid: the butter is difficultly separable from the curd, so that the cheese which it yields is rich and greasy. It affords 11·5 cream, 5·8 butter, 15·3 caseum, 4·2 milk-sugar *per cent.*

**COLOSTRUM.** When the glands begin to secrete milk, it is at first very different from what it becomes afterwards, and has been termed *colostrum*; it is more saline than perfect milk; and in the cow, yellow, thick, and sometimes streaked with blood; and coagulates when heated, like a serous secretion; it easily putrefies without becoming sour. Simon analysed the colostrum, and afterwards the milk of a woman, with the following results (*Die Frauenmilch nach ihrem Chem. und Physiologisch. Verhalten.* Berlin, 1838).

|                     | Colostrum. |      | Milk. |
|---------------------|------------|------|-------|
| Water.....          | 828.0      | .... | 887.6 |
| Solid matters ..... | 172.0      | .... | 112.4 |
| Fat .....           | 50.0       | .... | 25.3  |
| Caseine .....       | 40.0       | .... | 34.3  |
| Sugar of milk.....  | 70.0       | .... | 48.2  |
| Ash.....            | 3.1        | .... | 2.3   |

The following analyses of the colostrum of the cow, ass, and goat, are by Chevallier and Henry. (*Journ. de Pharm.*, xxv. 333 and 401.)

|                     | Cow.  |      | Ass.  |      | Goat. |
|---------------------|-------|------|-------|------|-------|
| Caseine .....       | 17.07 | .... | 12.30 | .... | 27.50 |
| Fat .....           | 2.60  | .... | 0.56  | .... | 5.20  |
| Sugar of milk ..... |       | .... | 4.30  | .... | 3.20  |
| Water .....         | 80.38 | .... | 82.84 | .... | 64.10 |

CREAM arises from the gradual separation of the lighter suspended matters, and the shallower the vessel the sooner it separates. When milk is kept for 5 or 6 days at the temperature of about  $33^{\circ}$ , it evolves nearly the whole of its cream; the residue looks like milk and water. By *churning*, cream is separated into *butter* and *butter-milk*; during this process, the temperature of the cream is slightly elevated, a little oxygen is absorbed, and acid produced; but this change is not essential to the separation of the butter, which takes place when air is excluded, and depends upon the rupture of the oil globules.

BUTTER is easily saponified, but the products of its saponification are very complicated: they have been especially examined by Chevreul (*Sur les Corps Gras*, and *Ann. Ch. et Ph.*, xxiii. 23), and by Bromeis and Lerch (*Ann. der Pharm.*, xlii. 66, and xlix. 212.) According to these authorities, butter contains margaric, butyroleic, butyric, capronic, caprylic, and capric acids, together with glycerine. The margarine, or margarate of glycerine, of butter, is solid at common temperatures; but the combinations of its other fatty acids with glycerine (constituting butyroleine, butyrine, capronine, capryline, and caprine) are fluid. According to Bromeis, 100 parts of butter contain about 68 parts of margarine, and 30 of butyroleine; the remainder consists of the glycerine-compounds of the other acids. Margaric and butyroleic acids are not volatile at the temperature at which butyric, and the other acids, assume the state of vapor, so that these latter may be separated by distillation from the former; they are further distinguished by their solubility in water, and by the comparative facility with which their glycerine compounds dissolve in alcohol. The margaric acid of butter is probably identical with that obtained from other fats, as already described (p. 1279), but the other acids require separate notice.

*Butyroleic Acid.*  $C_{34}H_{30}O_4 + HO$ . This acid is obtained from the *oleine* (butyroleate of glycerine) of butter, which remains after the separation of the margarine; this oleine is boiled with solution of potassa till it forms a clear soap, which is then decomposed by dilute sulphuric acid; the crude butyroleic acid thus separated, is then combined with oxide of lead, and the resulting lead-salt digested in ether, which takes up the butyroleate, and leaves margarate of lead. The *butyroleate of lead* is then decomposed by hydrochloric acid, and the separated oily acid carefully dehydrated, out of the contact of air, by

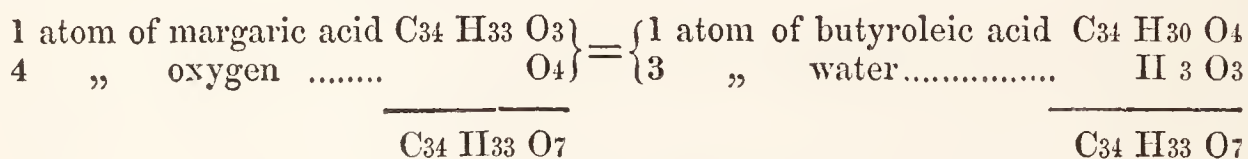


chloride of calcium. To obtain it colorless, it must be treated with blood-charcoal. (BROMEIS, *Ann. der Pharm.*, xlii. 55.)

Butyroleic acid is a clear, and generally slightly yellow liquid; its sp. gr. is 0·904. Heated a little above 212°, it becomes brown, and at higher temperatures evolves carburetted hydrogen, carbonic acid, and water, and a colorless oil distils over, leaving a little charcoal in the retort; but no sebacic acid is formed, as is the case with oleic acid. Exposed to air, butyroleic acid thickens in consequence of absorption of oxygen. It consists, in its isolated, or hydrated state, of

| Bromeis.         |    |     |       |        |       |                 |     |        |       |
|------------------|----|-----|-------|--------|-------|-----------------|-----|--------|-------|
| Carbon .....     | 34 | 204 | 74·18 | 74·41  | } = { | Anhydrous bu-   | 1   | 266    | 96·36 |
| Hydrogen .....   | 31 | 31  | 11·27 | 11·96  |       | tyroleic acid } |     |        |       |
| Oxygen .....     | 5  | 40  | 14·55 | 13·63  |       | Water .....     | 1   | 9      | 3·64  |
| <hr/>            |    |     |       |        |       |                 |     |        |       |
| Hydrated butyro- | }  | 1   | 275   | 100·00 | }     | 1               | 275 | 100·00 |       |
| leic acid .....  |    |     |       |        |       |                 |     |        |       |

*Butyroleates.* Some of these salts have been described by Bromeis; they have the general formula  $MO, + C_{34}H_{30}O_4$ . Bromeis thinks it probable that butyroleic acid may be a product of the oxidizement of margaric acid, and that by the farther action of oxygen it may pass into butyric, capronic, caprylic, and capric acids.



*Butyric Acid.*  $C_8H_7O_3 + HO = \overline{Bu} + HO$ . This acid may be obtained from several sources. 1. From *Butter*. Butter, purified by fusion and filtration, is kept for some days at a temperature of 66°, at which the greater part of the margarine concretes, leaving the other substances liquid. The liquid portion, separated by pressure and filtration, is agitated with alcohol, sp. gr. 0·796, which dissolves butyrine, capronine, capryline, and caprine, but a great part of the butyroleine remains undissolved. On distilling off the alcohol, the above mentioned fats remain, together with a little margarine and butyroleine: this residue is digested in a strong solution of caustic potassa, so as to form a mixture of butyrate, capronate, caprylate and caprate of potassa, with more or less margarate and butyroleate of potassa; these salts, being insoluble in the potassa-solution, separate, (leaving glycerine in the liquor,) and are to be decomposed by a solution of tartaric acid, when the margaric and butyroleic acids separate, but leave the volatile acids in aqueous solution. Tartaric acid is then added to this solution (in a stopped bottle) so as to throw down tartar; the solution is then poured off the tartar, and distilled; and if the distillate leaves any solid residue on evaporation, the distillation is repeated.

The distillate, which now contains butyric, capronic, caprylic, and capric acids, is to be saturated with baryta water, and evaporated by a gentle heat, to dryness. The butyrate and the capronate of baryta are very soluble, but the caprylate and the caprate, very difficultly soluble, in water; the dry mass is therefore digested in cold water, which takes up the former and leaves the latter salts. On carefully evaporating the

solution to a proper point, it concretes into a crystalline paste on cooling; the acicular crystals are chiefly capronate of baryta, and the mother-liquor when pressed out and evaporated, yields nacreous lamellar crystals of *butyrate of baryta*, which may be purified by recrystallization.

The difficultly soluble barytic salts, which remain after the abstraction of the butyrate and capronate of baryta, are to be dissolved in boiling water, and filtered hot: on cooling, fatty scales of caprate of baryta are formed, and the mother-liquor yields, on spontaneous evaporation, (which is best performed in the sunshine) crystals of caprylate of baryta. Both salts require to be purified by recrystallization. (CHEVREUL.)

Lerch proceeds as follows: (*Ann. der Pharm.*, xlix. 212.) Fresh butter is introduced into an alembic, where it is saponified, and the soap then decomposed by sulphuric acid; the head is then put on, and three-fourths of the liquor distilled over: water is then added to the residue, and the distillation repeated, and continued till the distillate is no longer acid. The acid distillate is then saturated with baryta-water, care being taken to exclude air, and evaporated in the alembic to about one-twentieth of its original volume; it is then transferred, whilst hot, into a glass retort, and evaporated to dryness. The dry residue consists of the above named barytic salts, and is to be treated as described.

2. *Formation of butyric acid by fermentation.* A moderately strong solution of sugar (indicating from  $8^{\circ}$  to  $10^{\circ}$  on Baumé's saccharometer, = sp. gr. 1.064, and *starch-sugar* is preferred,) is mixed with a quantity of pulverised chalk, amounting to about half the weight of the sugar, and to this mixture a portion of curd or caseine, or glutine, is added, equivalent to about 8 or 10 parts for every 100 of sugar. The whole is kept at a temperature of from  $75^{\circ}$  to  $85^{\circ}$ ; mucilaginous, and then lactic fermentation first ensue, and then carbonic acid and hydrogen are evolved, accompanying the *butyric fermentation*; these decompositions follow each other very irregularly, and their different stages cannot be controlled. After some weeks the evolution of gases ceases, and *butyrate of lime* is found in the liquor. (PELOUZE and GELIS. *Ann. Ch. et Ph.*, 3ème Sér., x. 434.)

The *butyrate of baryta* obtained by the first process, may be decomposed by sulphuric acid; for this purpose, 1 part of the butyrate may be mixed with 0.63 parts of sulphuric acid, sp. gr. 1.85, previously diluted with its weight of water; the butyric acid floats upon the surface, and must be dehydrated by chloride of calcium, and distilled. (CHEVREUL.) To decompose the *butyrate of lime*, it is distilled with slight excess of dilute hydrochloric acid; the distillate, which is an aqueous solution of butyric acid, is mixed with chloride of calcium, which abstracts the water and separates the butyric acid; this is left for some time in contact with pieces of fused chloride of calcium, and then poured off, and rectified from a tubulated retort with an inserted thermometer. When the temperature attains  $327^{\circ}$  the receiver is changed, and the pure acid then passes over. Scharling has obtained butyric acid as the result of the fermentation of *potatos*, (*Chem. Gaz.*, October, 1844,) and Wurtz has found it among the products of the putrefaction of fibrine. (*Comptes Rendus*, April, 1844.)

Butyric acid is a colorless, transparent, and very mobile fluid; its sp. gr. is .963, at  $60^{\circ}$ ; it has a pungent sour odor, resembling that of a mixture of



acetic acid and rancid butter; its taste is first pungent and sour, and then sweetish and slightly ethereal; it leaves a white spot upon the tongue; it does not congeal at  $0^{\circ}$ . but crystallizes at very low temperatures. Its boiling-point is about  $327^{\circ}$ , and the density of its vapor is 5.5. It is readily soluble in water, alcohol, ether, and wood-spirit; the density of a mixture of 2 parts of butyric acid and 1 of water is 1.00287; it is separated from its aqueous solution by some of the concentrated acids, especially by phosphoric acid; and also by the more soluble salts. It is miscible, without decomposition, with nitric acid. It burns with a bright blueish flame. When long kept in contact of air, it absorbs oxygen, and a part of it is decomposed. Subjected to the continuous action of chlorine, in the sun's rays, it yields *chlorobutyric acid*, and oxalic acid. When heated with sulphuric acid a slight decomposition ensues, but the greater part of it passes off unchanged. It consists, according to Pelouze and Gélis, of

|                       |   |     |    |     |        |       |              |   |   |     |    |     |        |
|-----------------------|---|-----|----|-----|--------|-------|--------------|---|---|-----|----|-----|--------|
| Carbon .....          | 8 | ... | 48 | ... | 54.54  | } = { | Anhydrous    | } | 1 | ... | 79 | ... | 89.77  |
| Hydrogen .....        | 8 | ... | 8  | ... | 9.09   |       | butyric acid |   |   |     |    |     |        |
| Oxygen .....          | 4 | ... | 32 | ... | 36.37  |       | Water.....   |   | 1 | ... | 9  | ... | 10.23  |
| <hr/>                 |   |     |    |     |        |       |              |   |   |     |    |     |        |
| Hydrated butyric acid | 1 |     | 88 |     | 100.00 |       |              |   | 1 |     | 88 |     | 100.00 |

*Butyrates.* These salts have been principally examined by Chevreul, Pelouze and Gélis, and Lerch. Their general formula is  $\text{MO}, \text{C}_8\text{H}_7\text{O}_3$ ; the equivalent of the anhydrous acid being 79. When dry, these salts are inodorous; but when moist, they smell of butter, and when acted upon by sulphuric acid evolve the odor of butyric acid; they are soluble in water, and most of them are crystallizable.

*Butyrate of Ammonia.*  $\text{NH}_4\text{O}, \overline{\text{Bu}}$ . The acid absorbs gaseous ammonia, and forms a salt which crystallizes in deliquescent needles.

*Butyrate of Potassa,*  $\text{KO}, \overline{\text{Bu}}$ , is a deliquescent and very difficultly crystallizable salt, soluble in less than its weight of water.

*Butyrate of Soda,*  $\text{Na O}, \overline{\text{Bu}}$ , resembles the potassa-salt, but is less deliquescent.

*Butyrate of Lime.*  $\text{CaO}, \overline{\text{Bu}}$ . This salt forms transparent acicular crystals, soluble in cold water, but diminishing in solubility with increase of temperature; so that, according to Chevreul, when the solution is raised to its boiling point, the greater part of the salt separates. It yields *butyrone* by dry distillation.

*Butyrate of Baryta.*  $\text{Ba O}, \overline{\text{Bu}}$ . According to Pelouze and Gélis this salt crystallizes in long transparent prisms containing 4 atoms of water of crystallization, and fusing at  $212^{\circ}$  without loss of weight. According to Lerch, when the crystals are formed by spontaneous evaporation in the direct rays of the sun, they are anhydrous, inodorous, unchangeable in the air, and not fusible in a water-bath: they sometimes form prisms, and are sometimes granular; they consist of

|                          |   |     |     |     |        |     |        |
|--------------------------|---|-----|-----|-----|--------|-----|--------|
| Carbon .....             | 8 | ... | 48  | ... | 31.10  | ... | Lerch. |
| Hydrogen .....           | 7 | ... | 7   | ... | 4.47   | ... | 4.55   |
| Oxygen .....             | 3 | ... | 24  | ... | 15.38  | ... | 15.33  |
| Baryta .....             | 1 | ... | 77  | ... | 49.05  | ... | 49.02  |
| <hr/>                    |   |     |     |     |        |     |        |
| Butyrate of baryta ..... | 1 |     | 156 |     | 100.00 |     | 100.00 |

*Butyrate of Strontia*,  $\text{Sr O}, \overline{\text{Bu}}$ , forms transparent needles, soluble in 3 parts of water at  $40^\circ$ .

*Butyrate of Magnesia*.  $\text{Mg O}, \overline{\text{Bu}}, + 5\text{HO}$ . This salt forms white micaceous crystals very soluble in water: they easily part with their water of crystallization.

*Butyrate of Zinc*.  $\text{Zn O}, \overline{\text{Bu}}$ . Evaporated *in vacuo* the solution of this salt yields brilliant lamellar crystals. During evaporation with heat, it gradually loses acid, and deposits basic compounds.

*Butyrate of Lead*,  $\text{Pb O}, \overline{\text{Bu}}$ , is best formed by evaporating a solution of oxide of lead in excess of butyric acid, *in vacuo*, over sulphuric acid; it forms silky needles. When a solution of acetate of lead is mixed with butyric acid, a heavy colorless liquid separates, which, dried at  $266^\circ$ , leaves a neutral butyrate. (PELOUZE and GELIS.)

When a solution of the preceding salt is digested with finely pulverized oxide of lead, and the filtered solution evaporated *in vacuo* over sulphuric acid, a difficultly soluble salt remains, which is a *tribasic butyrate of lead*,  $= 3\text{Pb O}, \overline{\text{Bu}}$ .

*Butyrate of Copper*.  $\text{Cu O}, \overline{\text{Bu}} + 2\text{HO}$ . When sulphate of copper is decomposed by butyrate of potassa a blue-green precipitate falls, which, dissolved in boiling water, yields transparent eight-sided prisms, having the above formula. When heated, they lose one atom of water, but the remaining atom cannot be expelled without decomposition.

*Butyrate of Mercury*.  $\text{Hg}_2 \text{O}, \overline{\text{Bu}}$ . A solution of butyrate of potassa throws down a white scaly precipitate from solutions of the suboxide of mercury, which resembles the acetate of the same base.

*Butyrate of Silver*.  $\text{Ag O}, \overline{\text{Bu}}$ . A concentrated solution of nitrate of silver yields a curdy precipitate with butyrate of baryta; when the solutions are dilute, they only become turbid, but on evaporation, dendritic crystals of the silver-salt are obtained. This salt has been analysed with the following results:

|                          |   |     |     |     |        | Lerch. | Iljenko and<br>Laskowski. |
|--------------------------|---|-----|-----|-----|--------|--------|---------------------------|
| Carbon .....             | 8 | ... | 48  | ... | 24.81  | ...    | 24.85                     |
| Hydrogen .....           | 7 | ... | 7   | ... | 3.37   | ...    | 3.63                      |
| Oxygen .....             | 3 | ... | 24  | ... | 12.27  | ...    | 11.96                     |
| Oxide of silver .....    | 1 | ... | 116 | ... | 59.55  | ...    | 59.56                     |
| <hr/>                    |   |     |     |     |        |        |                           |
| Butyrate of silver ..... | 1 |     | 195 |     | 100.00 |        | 100.00                    |

*Butyrate of Oxide of Ethyle. Butyric Ether*.  $\text{Ae O}, \overline{\text{Bu}}, = \text{C}_{12}\text{H}_{12}\text{O}_4$ . This compound is instantly formed when 2 parts of butyric acid, 2 of alcohol, and 1 of sulphuric acid are mixed; it rises to the surface, and is to be washed, and rectified over chloride of calcium. It has an agreeable ethereal odor, and is said to communicate the flavor of rum to grain-spirit.

*Butyrate of oxide of Methyle. Butyro-methylic Ether*.  $\text{Me O}, \overline{\text{Bu}}, = \text{C}_{10}\text{H}_{10}\text{O}_4$ . This ether is formed as the preceding: it has the odor of wood-spirit.

BUTYRONE,  $\text{C}_7\text{H}_7\text{O}$ , is the product of the distillation of *butyrate of lime*, from which it is obtained to the amount of about 40 per cent. in its crude state. The boiling-point of this crude butyrene becomes stationary between  $290^\circ$  and  $295^\circ$ , and pure butyrene distils over: it is a colorless



limpid liquid, of a penetrating and peculiar odor; its sp. gr. is 0·83: its boiling-point about  $292^{\circ}$ : in the cold mixture of solid carbonic acid and ether it becomes a crystalline mass; it is almost insoluble in water, but soluble in all proportions in alcohol: it burns with a bright flame: it gradually absorbs oxygen without becoming discolored: it is violently acted upon, and inflamed by chromic acid. The density of its vapor is 3·96, two volumes of which are represented by the above formula. The conversion of butyrate of lime into carbonate of lime and butyrone is as follows:—  
 $\text{Ca O, C}_8\text{H}_7\text{O}_3 = \text{Ca O, CO}_2 + \text{C}_7\text{H}_7\text{O}.$

*Nitrobutyronic Acid.*  $\text{C}_7\text{H}_6\text{O, NO}_4, + 2\text{HO}.$  When butyrone is heated with its volume of nitric acid, torrents of red vapor are evolved, which, conducted through water, deposits a volatile liquid of an ethereal odor. The residue in the flask is then well washed, by which an oily liquid, heavier than water, is obtained, of a yellow color, and not congealing in the mixture of solid carbonic acid and ether. It has an aromatic odor and sweetish taste; it burns with a reddish flame; is soluble in all proportions in alcohol; and combines with bases, forming crystallizable salts. In its formation, 1 equivalent of nitrous acid replaces 1 of hydrogen in the butyrone: it is a bibasic acid.

*Nitrobutyronate of Potassa,*  $\text{KO, HO,} + \text{C}_7\text{H}_6\text{O, NO}_4,$  is formed by mixing alcoholic solution of potassa with the acid; the mixture concretes, and, washed with alcohol, yields small yellow scales, which inflame with a kind of explosion when heated to  $212^{\circ}$ : they are nearly insoluble in alcohol, but soluble in about 20 parts of water: this solution gives a yellow precipitate with the salts of lead and of silver; and a dingy-green with those of copper. The *nitrobutyronate of lead* has 2 equivalents of base; so has that of *silver*; but the latter, when boiled, deposits 1 equivalent of oxide, which is replaced by 1 of water, to form a crystallizable salt:  $2\text{AgO,} + \text{C}_7\text{H}_6\text{O, NO}_4,$  becoming  $\text{AgO, HO,} + \text{C}_7\text{H}_6\text{O, NO}_4.$

**CHLOROBUTYRONE.** Distilled with perchloride of phosphorus, butyrone forms phosphoric and hydrochloric acids, and a peculiar colorless liquid, lighter than, and insoluble in water, soluble in alcohol, and inflammable. Its analysis gives  $\text{C}_{14}\text{H}_{13}\text{Cl} = 4$  vols. of vapor. (CHANCEL. *Ann. Ch. et Ph.*, Oct. 1844.)

**CAPRONIC ACID. CAPROIC ACID.**  $\text{C}_{12}\text{H}_{11}\text{O}_3 + \text{HO}.$  This acid, originally discovered by Chevreul in butter, has also been found in coconut oil by Fehling. It has already been stated that amongst the volatile acids of butter, the butyric and the capronic acids form very soluble barytic compounds, and the mode of separating the capronate from the butyrate of baryta has been adverted to. Of the former salt, 100 parts require for decomposition about 30 of sulphuric acid, sp. gr. 1·8, diluted with its weight of water; after some hours, the capronic acid separates upon the surface; it requires to be rectified over chloride of calcium. The mode of obtaining this acid from the soap of coconut oil has been described by Fehling, (*Ann. der Pharm.*, liii. 399,) and Iljenko and Laskowski have detected it in Limburgh cheese. (*Ibid.*, lv. 83.)

Capronic acid is a transparent oily fluid; its odor resembles that of sweat; it is very sour, and has a slightly ethereal flavor, leaving a white spot upon the tongue: at very low temperatures it crystallizes; it requires about 100 parts of water for its solution, but alcohol dissolves it in all

proportions. It burns with a bright flame. By the destructive distillation of the capronates, it is said to yield *capronone* =  $C_{11}H_{11}O$ , and  $CO_2$ . In its isolated state it is a *hydrate*, containing

|                               |    |      |     |      | Fehling. |      |        |       |                              |       |       |             |      |       |        |      |      |
|-------------------------------|----|------|-----|------|----------|------|--------|-------|------------------------------|-------|-------|-------------|------|-------|--------|------|------|
| Carbon .....                  | 12 | .... | 72  | .... | 62.07    | .... | 62.03  | } = { | Anhydrous ca-<br>pronic acid | 1     | ....  | 107         | .... | 92.24 |        |      |      |
| Hydrogen .....                | 12 | .... | 12  | .... | 10.34    | .... | 10.43  |       |                              |       | } = { | Water ..... | 1    | ....  | 9      | .... | 7.76 |
| Oxygen .....                  | 4  | .... | 32  | .... | 27.59    | .... | 27.54  |       |                              |       |       |             |      |       |        |      |      |
| <hr/>                         |    |      |     |      | <hr/>    |      |        |       |                              | <hr/> |       |             |      |       |        |      |      |
| Hydrated ca-<br>pronic acid } | 1  |      | 116 |      | 100.00   |      | 100.00 |       |                              |       | 1     |             | 116  |       | 100.00 |      |      |



by phosphoric acid. One hundred parts of the salt require 48 of sulphuric acid, diluted with its weight of water; or 84 of vitrified phosphoric acid dissolved in 240 parts of water. The capric acid is distilled, after having been digested upon chloride of calcium. This acid concretes at about 60°; at 65° it liquifies, and may be cooled in close vessels down to 52° without solidification, but the moment air is admitted it concretes. It has a rank goat-like odor, and tastes very sour, and afterwards slightly sweet; its sp. gr. is 0·91; it boils at about 520°; the density of its vapor is 5·98. It is almost insoluble in water, but abundantly soluble in alcohol and ether. It consists of

|                            |    |     |     |     |        |       |                             |   |     |        |     |       |
|----------------------------|----|-----|-----|-----|--------|-------|-----------------------------|---|-----|--------|-----|-------|
| Carbon .....               | 20 | ... | 120 | ... | 69·18  | } = { | Anhydrous capric acid ..... | 1 | ... | 163    | ... | 94·77 |
| Hydrogen .....             | 20 | ... | 20  | ... | 11·62  |       |                             |   |     |        |     |       |
| Oxygen .....               | 4  | ... | 32  | ... | 19·20  |       |                             |   |     |        |     |       |
| <hr/>                      |    |     |     |     |        |       |                             |   |     |        |     |       |
| Hydrated capric acid ..... | {  |     | 1   | 172 | 100·00 |       |                             | 1 | 172 | 100·00 |     |       |

Caprates. Caprate of Baryta, Ba O, C<sub>20</sub> H<sub>19</sub> O<sub>3</sub>, is difficultly crystallizable in small acicular and dendritic crystals, very sparingly soluble even in boiling water, and permanent in the air. When its solution is kept for some time it becomes turbid, and acquires the odor of Roquefort cheese. Its components are

|                        |    |     |     |     |        | Lerch. | Iljenko and Laskowski. |
|------------------------|----|-----|-----|-----|--------|--------|------------------------|
| Carbon .....           | 20 | ... | 120 | ... | 50·00  | 50·26  | 49·97                  |
| Hydrogen .....         | 19 | ... | 19  | ... | 7·91   | 7·91   | 7·85                   |
| Oxygen .....           | 3  | ... | 24  | ... | 10·00  | 10·13  | 10·50                  |
| Baryta .....           | 1  | ... | 77  | ... | 32·09  | 31·70  | 31·68                  |
| <hr/>                  |    |     |     |     |        |        |                        |
| Caprate of baryta .... | 1  |     | 240 |     | 100·00 | 100·00 | 100·00                 |

VACCINIC ACID. Lerch has given this name to a peculiar modification of the volatile acids of butter, which is occasionally obtained when the more soluble portion of the saline mass obtained by neutralizing them with baryta, instead of yielding distinct crystals of capronate and butyrate of baryta, affords groups of prismatic crystals containing a distinct acid; but when these crystals, after having been long exposed to air, are dissolved in water, their solution yields capronate and butyrate, as usual. This acid probably is bibasic, and consists of C<sub>20</sub> H<sub>18</sub> O<sub>6</sub>, being derived from a combination of the elements of the butyric and capronic acids = C<sub>8</sub> H<sub>7</sub> O<sub>3</sub> + C<sub>12</sub> H<sub>11</sub> O<sub>3</sub>. A similar occasional peculiarity in these acids of butter was observed by Chevreul, but the causes which produce it have not been ascertained. The summer of 1842, when the butyric and caproic acids was replaced by the vaccinic, was remarkably dry; in 1843 caprate and butyrate of baryta were obtained as usual, and there was no trace of the vaccinate.

SUGAR of MILK. LACTINE. LACTOSE. C<sub>12</sub> H<sub>10</sub> O<sub>10</sub> + 2HO, or C<sub>24</sub> H<sub>24</sub> O<sub>24</sub>. This substance is first described by Bartholetti, (*Encyclopædia Hermetico-dogmatica*, Bologna, 1619,) under the name of *Manna, seu nitrum seri lactis*. “The person who contributed to make sugar of milk generally known, was Ludovico Festi, who gave it out as an invention of his own, and sold it as a remedy in gout and other diseases. He was a physician in Venice, where he died, in 1707. After his death, Valisneri published the process which Festi employed in extracting this sugar

from whey." (THOMSON. *Chem. of Animal Bodies*, 131.) This substance, which hitherto has only been found in milk, is largely manufactured, as an article of food, in Switzerland. To obtain it the milk is coagulated by a little dilute sulphuric acid, and the resulting *whey* is evaporated till the sugar crystallizes; it is whitened by animal charcoal and repeated crystallization.

*Lactine* crystallizes in white four-sided prisms, generally terminated by four-sided pyramids, and having a lamellar fracture. Its sp. gr. is 1.543. It is hard and somewhat gritty, and only slightly sweet. It is slowly soluble, without forming a syrup, in about 13 parts of boiling, and 6 of cold water. It is almost insoluble in alcohol, which therefore throws it down from its aqueous solution; it is insoluble in ether. The elements of *anhydrous lactine* are

|                   |    |     |     |     |        |                          |   |     |     |     |       |
|-------------------|----|-----|-----|-----|--------|--------------------------|---|-----|-----|-----|-------|
| Carbon .....      | 12 | ... | 72  | ... | 44.44  | Anhydrous lactine ...    | 1 | ... | 162 | ... | 90.0  |
| Hydrogen .....    | 10 | ... | 10  | ... | 6.17   |                          |   |     |     |     |       |
| Oxygen .....      | 10 | ... | 80  | ... | 49.39  | Water .....              | 2 | ... | 18  | ... | 10.0  |
| <hr/>             |    |     |     |     |        |                          |   |     |     |     |       |
| Anhydrous lactine | 1  |     | 162 |     | 100.00 | Crystallized lactine.... | 1 |     | 180 |     | 100.0 |

The ultimate elements of *crystallized lactine* are

|                      |    |     |     |     |        | Gay-Lussac and |          |            |         |
|----------------------|----|-----|-----|-----|--------|----------------|----------|------------|---------|
|                      |    |     |     |     |        | Prout.         | Thenard. | Berzelius. | Liebig. |
| Carbon .....         | 12 | ... | 72  | ... | 40.00  | 40.00          | 38.835   | 39.574     | 40.00   |
| Hydrogen .....       | 12 | ... | 12  | ... | 6.67   | 6.67           | 7.341    | 7.167      | 6.73    |
| Oxygen .....         | 12 | ... | 96  | ... | 53.33  | 53.33          | 53.824   | 53.259     | 53.27   |
| <hr/>                |    |     |     |     |        |                |          |            |         |
| Crystallized lactine | 1  |     | 180 |     | 100.00 | 100.00         | 100.000  | 100.000    | 100.00  |

By digestion in very dilute sulphuric acid lactine is converted into glucose. It does not appear susceptible of fermentation under the direct influence of yeast, nevertheless it is well known that the Tartars procure a spirituous liquor from mare's milk, termed *koumiss*, (GRIEVE and GUTHRIE, *Edinb. Phil. Trans.*, vols. i. and ii.,) and it is stated by Dr. Thomson, on the authority of Sir John Sinclair, that a similar liquor is prepared from cows' milk in Orkney and Shetland. Schill, who has given a detailed account of this process, (*Ann. der Pharm.*, xxxi. 152,) says that 36 parts of alcohol may be obtained from 100 of sugar of milk. In this fermentation the first change which ensues is the souring of the milk, and this process is no doubt connected with the transition of lactine into glucose (grape or starch-sugar); indeed it has long been known that caseine is capable of thus transmuting *cane-sugar*.

The conversion of lactine into glucose by the protracted action of dilute acids, is well shown by the non-action of the former upon an alkaline solution of tartrate of copper; whereas after having been long in the contact of acids, or when boiled with a little dilute acid, the presence of grape-sugar is indicated by the peculiar precipitate above described (p. 1183). According to Vogel, the weight of grape-sugar thus produced, falls short of that of the original milk-sugar; (*Annales de Chimie*, lxxxii. 148;) but 100 parts of sugar of milk, by combining with 2 atoms of water, ought to produce 109.8 parts of grape-sugar. (LIEBIG.)

When lactine is gently heated (to 248°), it loses, according to Berzelius, 5.3 per cent. of water, without fusion; at a temperature of 280° to 300°, it fuses and becomes anhydrous, losing, therefore, 10 per cent. of water, but at that temperature it becomes discolored, and exhibits



symptoms of decomposition; it loses its sweetness, and becomes uncrySTALLIZABLE, and very soluble in water. By dry distillation, it affords the usual products of this class of compounds.

By nitric acid, lactine is converted into *mucic acid* (p. 1196), hence the term *saclactic* (lactinic?) *acid* applied to that compound; 1 atom of anhydrous lactine may thus yield 1 atom of hydrated mucic acid, by the assumption of 6 atoms of oxygen;  $C_{12}H_{10}O_{10} + O_6 = C_{12}H_{10}O_{16}$ ; so that it is a case of simple oxidizement. (LIEBIG. *Poggend. Ann.*, xxxi. 149.)

By the action of the stronger acids lactine yields *ulmic acid*.

When lactine is triturated with slaked lime and water, heat is evolved, and a brown liquid formed, from which alcohol precipitates a thick, brown, and bitterish syrup, which is deliquescent, and precipitates metallic solutions. Acetate of potassa is at the same time formed. (VOGEL.) Under the protracted action of caustic alkaline solutions, lactine yields glucic, and ultimately melassic acid. (PELIGOT. *Erdmann and Marchand's Journ.*, xv. 96.)

Pulverised lactine absorbs ammonia; it also absorbs hydrochloric gas. According to Brendecke (*Archiv. für Pharm.*, xxix. 88; LÖWIG, *Chem. der Org. Verb.*, i. 394), 1 part of caustic potassa in 3 parts of water dissolve 7 parts of lactine, forming a thick clear liquid, from which alcohol throws down a definite *lactide of potassa*  $= KO, HO, C_{12}H_{10}O_{10}$ . He has obtained similar compounds with soda, lime, and baryta.

When oxide of lead is digested in a solution of lactine at a temperature not exceeding  $140^{\circ}$ , three compounds are formed; one of these, which is *basic*, forms a heavy granular powder, containing 82 *per cent.* of oxide. A white viscid compound remains suspended in the liquid, which, when dried, becomes yellowish and translucent; this is the *neutral* lactide; it contains 63.7 *per cent.* of oxide. On adding ammonia to the liquid, a further portion of the neutral compound falls, and on filtering and evaporating the mixture, a transparent gum-like mass remains, containing 18 *per cent.* of oxide. (BERZELIUS.)

LACTIC ACID.  $C_6H_5O_5 + HO; = \overline{L} + HO$ . This acid, as its name imports, was originally discovered in *sour milk* (SCHEELE, *Opusc.*, ii. 101); it was then recognized by Berzelius, in certain animal fluids; and afterwards by Braconnot, as a product, along with acetic acid, of the sour fermentation of rice-meal, wheat-paste, the juice of the beet-root, and other vegetable substances; he gave it the name of *Nanceic acid*, from Nancy, the place of his residence. (*Annales de Chimie*, LXXXV. 84.) It has also been termed *Zumic acid* (from ζυμη, *leaven*). It was at one time supposed to be a compound of acetic acid with organic matter, a conclusion disproved by Pelouze and Jules Gay-Lussac. (*Ann. Ch. et Ph.*, Lii. 410.) It has been found by Coriol, combined with lime and magnesia, in the fermented infusion of *nux vomica* (*Journ. de Pharm.*, xix. 155, 373), and exists, according to Liebig, in the juice of animal flesh.

Lactic acid may be obtained, (1,) from *sour milk*. Sour whey is evaporated to one-sixth of its original weight and filtered; a little lime is added to the filtrate to precipitate phosphoric acid, and excess of lime having been removed by oxalic acid, and filtration, the liquor is evaporated to the consistence of syrup, and the lactic acid extracted by means



of alcohol. The alcoholic solution is evaporated, the residue diluted with water, saturated with carbonate of lead, and filtered. The resulting solution of lactate of lead is then precipitated by sulphate of zinc, so as to form sulphate of lead and lactate of zinc; the filtered solution of the latter salt is crystallized by evaporation, and the zinc-salt, purified by crystallization, is dissolved in water, and precipitated by baryta-water, so as to form lactate of baryta: this latter salt is then decomposed by dilute sulphuric acid, the filtrate is evaporated, and the residue digested in ether; on evaporating this ethereal solution, pure lactic acid remains. (MITSCHERLICH. *Ann. der Pharm.*, vii. 47.) (2.) As lactic acid is the result of the fermentation of lactine, the ferment being altered caseine, the following process for the production of that acid is adopted by Frémy and Boutron-Charlard. (*Ann. der Pharm.*, xxix. 181.) A solution of about half a pound of sugar of milk is added to 6 pints of skimmed milk, and left in an open vessel at a temperature between  $60^{\circ}$  and  $70^{\circ}$ . As soon as the liquor becomes sour it is neutralized by bicarbonate of soda; in a few days it becomes again sour, and is again neutralized, and this operation is repeated till the whole of the lactine is acidified: the liquor is then heated up to its boiling-point, filtered, and gently evaporated to the consistence of syrup; the residue is treated with warm alcohol, which takes up the lactate of soda, and this alcoholic solution is decomposed by sulphuric acid, which throws down sulphate of soda, and leaves lactic acid in solution; this solution, mixed with water and saturated with carbonate of lime, yields lactate of lime, on evaporation, from which pure lactic acid may be obtained by careful decomposition by oxalic acid. (3.) Lactic acid may be obtained by exposing the expressed juice of beet-root to a temperature between  $75^{\circ}$  and  $85^{\circ}$ ; in some days, what has been termed *viscous fermentation* comes on, and continues for about two months; when this has ceased, the juice is evaporated to the consistency of syrup, during which crystals of *mannite* separate: it is then treated by alcohol, which takes up lactic acid, and which may be to a certain extent purified by evaporation, and solution of the residue in water; a portion of insoluble impurity remains: this aqueous solution of the impure lactic acid is then saturated by carbonate of zinc; the soluble lactate of zinc is separated by filtration, and crystallized; it is then redissolved in water, boiled with animal charcoal, and filtered whilst hot: on cooling, the *lactate of zinc* separates in white crystals, which are washed with alcohol, decomposed by baryta, and the lactate of baryta, which is soluble, is decomposed by sulphuric acid. (4.) The formation of lactate of lime in the process for obtaining butyric acid, has already been mentioned. For the preparation of *lactic acid* the process may be conducted as follows (BLÜCHER, *Poggend. Ann.*, Lxiii. 425):—6 lbs. of raw sugar is dissolved in 12 pints of water and added to 2 gallons of skimmed milk previously mixed with 4 lbs. of prepared chalk. This mixture is exposed in a loosely covered vessel, to a temperature between  $60^{\circ}$  and  $70^{\circ}$ , under occasional stirring; in a fortnight or three weeks it is found converted into a pasty mass of lactate of lime, which may at once be pressed, and purified by solution and crystallization. In this, as in the butyric fermentation, the liquor must always be kept neutral, and this is effected by the presence of the carbonate of lime, the excess of which in no way interferes with the process, and being at once added, does



away with the necessity of repeated additions of base, as where carbonate of soda is used. The purified lactate of lime is decomposed by oxalic acid, as above described.

Pure lactic acid, after it has been exposed *in vacuo* till it no longer loses water, is a colorless liquid of the consistence of syrup; its sp. gr., at 68°, is 1.215; it is inodorous, and very sour, but its acidity rapidly diminishes on the addition of water; it is deliquescent, and miscible in all proportions with water and alcohol; it is less soluble in ether. It readily dissolves phosphate of lime, and it coagulates albumine. Its aqueous solution undergoes no change. When mixed with cold milk it produces no change, but when the milk is boiled, the presence of a very small trace of lactic acid induces coagulation. When the acid, in the state of hydrate just described, is kept for some time at a temperature of 266°, it loses an atom of water, and remains in the state of a fusible solid, of a pale yellow color and bitter taste, almost insoluble in water, but soluble in alcohol and in ether. In this state it has the same composition as when in combination with oxide of zinc, and may therefore be regarded as *anhydrous lactic acid*; it consists of

|                            |   |     |    |     |        | Mitscherlich. | Pelouze.   |
|----------------------------|---|-----|----|-----|--------|---------------|------------|
| Carbon.....                | 6 | ... | 36 | ... | 44.89  | .... 44.481   | .... 45.50 |
| Hydrogen .....             | 5 | ... | 5  | ... | 6.11   | .... 6.168    | .... 6.32  |
| Oxygen .....               | 5 | ... | 40 | ... | 49.00  | .... 49.351   | .... 48.18 |
| <hr/>                      |   |     |    |     |        |               |            |
| Anhydrous lactic acid .... | 1 |     | 81 |     | 100.00 | 100.000       | 100.00     |

The components of the *hydrated acid* are,

|                      |   |     |    |     |        |       |                       |   |     |    |     |       |
|----------------------|---|-----|----|-----|--------|-------|-----------------------|---|-----|----|-----|-------|
| Carbon .....         | 6 | ... | 36 | ... | 40.00  | } = { | Anhydrous lactic acid | 1 | ... | 81 | ... | 90.0  |
| Hydrogen .....       | 6 | ... | 6  | ... | 6.67   |       | Water .....           | 1 | ... | 9  | ... | 10.0  |
| Oxygen .....         | 6 | ... | 48 | ... | 53.33  |       |                       |   |     |    |     |       |
| <hr/>                |   |     |    |     |        |       |                       |   |     |    |     |       |
| Hydrated lactic acid | 1 |     | 90 |     | 100.00 |       |                       | 1 |     | 90 |     | 100.0 |

*Lactates.* The greater number of these salts are soluble in water and crystallizable. Heated with 5 or 6 parts of sulphuric acid, these salts effervesce, and evolve carbonic oxide; the mixture becomes brown, and deposits, when acted upon by water, a substance having the properties of ulmic acid: no formic acid is formed. The acetates are decomposed by lactic acid. The general formula of lactic salts is MO, C6 H5 O5. They have been principally studied by Pelouze and Jules Gay-Lussac. (*Ann. Ch. et Ph.*, xlii. 421. *Ibid.* 3ème Sér., Mars, 1845.)

*Lactate of Ammonia.* NH4 O, C6 H5 O5. This salt forms deliquescent prismatic crystals; exposed to the air they lose ammonia and become acid.

*Lactate of Potassa,* and *Lactate of Soda,* are very soluble and difficultly crystallizable.

*Lactate of Lime.* Ca O, C6 H5 O5, + 6HO. This salt is easily soluble in boiling water, and crystallizes, on cooling, in groups of short prisms; it is more soluble in alcohol than in water, and is thrown down by ether from its alcoholic solution in the form of a crystalline powder. The alcoholic solution is precipitated by phosphoric acid; but phosphate of lime is decomposed by an aqueous solution of lactic acid. The production of this salt in lactic fermentation has been above mentioned. When heated to its point of fusion it loses 5 atoms of water of crystallization. Lactate of lime may be obtained from the *nux vomica*. (CORIOL.)



*Lactate of Baryta*,  $\text{Ba O, C}_6\text{H}_5\text{O}_5$ , is obtained by decomposing lactate of zinc by baryta-water. When evaporated it forms a gum-like uncrystallizable mass.

*Lactate of Magnesia*.  $\text{Mg O, C}_6\text{H}_5\text{O}_5, + 3\text{HO}$ . This salt may be obtained in white shining crystals, which are efflorescent, and require 10 parts of water for their solution.

*Lactate of Manganese*,  $\text{Mn O, C}_6\text{H}_5\text{O}_5, + 4\text{HO}$ , is a crystallizable and efflorescent salt, of a pale red color.

*Lactate of Iron*.  $\text{Fe O, C}_6\text{H}_5\text{O}_5, + 3\text{HO}$ . Iron dissolves in dilute lactic acid, with the evolution of hydrogen, and the solution yields white acicular crystals, difficultly soluble in water, and permanent in the air. Wöhler prepares this salt by mixing iron filings and powdered milk-sugar with sour milk or whey, (2 lbs. of sour whey, 1 oz. of milk-sugar, 1 oz. of iron,) at a temperature of about  $100^\circ$ . The iron dissolves in the free lactic acid with slight evolution of hydrogen, while fresh lactic acid is formed by the action of the caseine upon the milk-sugar, fresh portions of which are occasionally added: when the salt of iron begins to be deposited, the whole mass is heated to boiling, and filtered while hot, into a vessel which can be closed: on cooling, the lactate forms a greenish crystalline crust of small prismatic crystals, which continues depositing for several days: these are collected, washed with cold water, and dried quickly upon blotting-paper by a gentle heat. The salt may be purified by recrystallization from its solution in boiling water.

The *lactate of peroxide of iron* is a brown deliquescent salt.

*Lactate of Zinc*.  $\text{Zn O, C}_6\text{H}_5\text{O}_5 + 3\text{HO}$ . This salt crystallizes in four-sided prisms, terminated by obliquely truncated summits; it is difficultly soluble in water and in alcohol; it sustains a heat of  $470^\circ$  without decomposition: it is probably isomorphous with the magnesian, and with the iron-salt.

*Lactate of Cadmium* forms delicate white needles, soluble in 9 parts of cold, and 4 of boiling water, and insoluble in alcohol.

*Lactate of Copper*.  $\text{Cu O, C}_6\text{H}_5\text{O}_5, 2\text{HO}$ . This salt forms blue prisms, efflorescent, and insoluble in alcohol. It loses its water of crystallization at  $248^\circ$ .

*Lactate of Lead* resembles the salt of baryta; it is deliquescent, and yields basic compounds when its solution is boiled with oxide of lead.

*Lactate of Silver* forms white acicular crystals, very soluble, and speedily blackened by light.

*Lactate of Alumina* is very soluble and difficultly crystallizable.

**LACTIDE. PYROLACTIC ACID.**  $\text{C}_6\text{H}_4\text{O}_4$ . This compound was discovered by J. G. Lussac and Pelouze; it is the result of the dry distillation of lactic acid, and is accompanied by acetone, and a peculiar compound, *lactone*.

Lactide forms a white sublimate, which may be purified by solution in hot alcohol, from which it crystallizes on cooling, in white rhomboidal tables. It has a slightly acid taste: it fuses at  $225^\circ$ , and at  $480^\circ$  boils and forms an inflammable vapor, which condenses in crystals upon cold bodies. Lactide is very slowly soluble in pure water, and when this solution is evaporated *in vacuo*, it leaves common lactic acid, reassuming the atom of constituent water which it had lost in its formation. When lactide is long exposed to damp air it also reverts to lactic acid.



Lactide combines with dry ammonia to form *lactamide*,  $= \text{NH}_3, \text{C}_6\text{H}_4\text{O}_4$ , a compound in which the ordinary tests fail to discover ammonia. It crystallizes in rectangular prisms from its alcoholic solution.

LACTONE,  $\text{C}_{10}\text{H}_9\text{O}_5$ , is a colorless liquid, separable, by careful distillation, from the products of the dry distillation of lactic acid; it has an aromatic odor and a hot taste, and is lighter than, and soluble in water; it boils at  $188^\circ$ , and burns with a blue flame.

### § III. BILE. BILIARY CONCRETIONS. CHOLESTERINE. INTESTINAL CONCRETIONS. AMBERGRIS. CERUMEN. BRAIN, AND NERVOUS MATTER. EGGS.

BILE. This important secretion which is separated from venous blood in the liver, has been the subject of repeated analyses which have led to very discrepant results, chiefly in consequence of confounding products with educts. The old chemists (CADET. *Mém. de l'Acad.*, 1767, p. 471,) regarded bile as a saponaceous compound, in which an organic acid was combined with soda; but their successors represented it under a much more complex aspect, till at last, between 20 and 30 proximate components were assigned to it. But the researches of Demarçay have shown that there are strong grounds for returning to the ancient view, and that the supposed complexity of bile has arisen from the cause just adverted to; that it is in fact a *soda-soap*, which may be decomposed and recomposed, and that the other substances, normally present in it, are only in small and variable quantity. (*Ann. Ch. et Ph.*, Lxvii. 177. *Ann. der Pharm.* xxvii. 270.) The bile of the ox (ox-gall) has chiefly been experimented upon; but Frommherz and Gugert have examined human bile (*Schweigger's Journ.* v. 1); Tiedemann and Gmelin that of several birds (*Über die Verdauung*); Berzelius that of some reptiles; and Strecker and Gundelach that of the hog (*Ann. Ch. et Ph.*, 3ème Sér., xxii. 38).

Bile, in its ordinary state, varies in appearance; from the ox it is generally of a dingy green color, transparent, and viscid; it has a peculiar odor, and a nauseously bitter, and at the same time, slightly sweet taste. Its mean sp. gr. is 1.025. It has a slightly alkaline reaction, and mixes, in all proportions, with water.

When bile is evaporated to dryness upon a water-bath, it leaves about 10 per cent. of solid matter. This solid residue consists chiefly of *choleate of soda, fatty matters, mucus, and coloring matter*. The fatty matters (cholesterine, &c.,) may be abstracted by ether, after which, alcohol takes up the choleate of soda and coloring matter, and leaves mucus. The coloring-matter may be separated by digesting animal charcoal in the alcoholic solution, which, when thus rendered colorless, yields the choleate of soda on evaporation. In this way, therefore, the principal components of the bile, namely, choleate of soda, fatty matter, coloring matter, and mucus, may be separated.

The *choleate of soda* may, according to Verdeil, (*Turner's Chem.*, p. 1295,) be obtained in small acicular crystals, by the careful evaporation of its alcoholic solution. If this be carried to dryness, it remains in the form of a yellowish gum-like mass, soluble in water and in alcohol. Its solution is rendered turbid by sulphuric, and by hydrochloric acid, and is

amply precipitated by basic acetate of lead. The formula of choleate of soda, is, according to the analysis of Verdeil,  $\text{Na O}$ ,  $\text{C}_{44} \text{H}_{40} \text{O}_9 \text{N S}$ .

*Choleic Acid.*  $\text{C}_{44} \text{H}_{40} \text{O}_9 \text{N S} + \text{H O}$ . This compound may be obtained (1) by adding acetate of lead to a solution of bile in 10 or 15 parts of water, and afterwards a little ammonia. The resulting precipitate is gently heated so as to fuse it; the liquor is then poured from it, and it is triturated and washed with a little water, and afterwards treated with boiling alcohol, which dissolves an acid salt, leaving a basic salt, and a compound of coloring matter and oxide of lead. The alcoholic solution, decomposed by sulphuretted hydrogen, filtered, and evaporated to dryness, leaves a brown resinous magma, from which, fatty matters (margaric acid and cholesterine) must be separated by ether; it is then redissolved in cold weak alcohol, filtered, and evaporated to dryness: the remaining choleic acid is slightly contaminated by soda, sulphur, and margaric acid. (DEMARÇAY.) (2.) 10 parts of bile (previously purified as above described, by alcohol,) are dissolved in 100 parts of water; to this, 2 parts of sulphuric acid, previously diluted with 10 parts of water, are added, and the mixture evaporated by a gentle heat; as soon as it becomes somewhat turbid, and oleaginous drops appear upon its surface, it is set aside for 8 or 10 hours, when the choleic acid separates in the form of a green oily magma; the liquor is poured off and filtered, to separate the cholesterine and margaric acid which float upon the surface, and is again evaporated as before, when a fresh portion of choleic acid is deposited. These deposits are then washed with a little water, and dissolved in alcohol, and a few drops of baryta water are carefully added to precipitate a little adhering sulphuric acid; the filtered liquor is then evaporated to the consistence of syrup, and shaken with ether to remove any remaining traces of margaric acid; the ether is then separated, and evaporation carried on upon a water-bath, till the choleic acid becomes pasty, when it is transferred, whilst warm, under the receiver of an air-pump, which is to be rapidly exhausted; in this way the mass swells up from loss of water, and ultimately remains in the form of a dry, yellow, spongy and friable mass. It generally retains a trace of soda, and of baryta. (DEMARÇAY.) (3.) 8 parts of purified bile are dissolved in alcohol, to which 1 part of effloresced (monohydrated) oxalic acid is added; the mixture is boiled, and then set aside, when crystals of oxalate of soda gradually separate from it. The filtered liquor is then diluted with a little water and digested upon carbonate of lead, so as to abstract any remaining oxalic acid, and sulphuretted hydrogen is then passed through it to remove any residuary lead. The filtered liquor is then evaporated upon a water-bath, and the remaining choleic acid carefully dried. (LIEBIG.) For the final purification of choleic acid it may be dissolved in a small proportion of alcohol, and precipitated by ether.

Choleic acid is an amorphous yellowish gum-like substance, somewhat deliquescent, and of a bitter taste; it has an acid reaction. It is soluble in water and in alcohol, but not in ether. It is partially precipitated from its aqueous solution, by the mineral acids, but in excess they redissolve it. When combined with soda it reproduces a substance having all the characters of the original choleate of the bile. When pure choleic acid is heated upon platinum foil, it leaves a bulky charcoal, which finally burns away without residue; but if the choleic acid retain choleate of



soda, it of course leaves an alkaline ash. Acid choleate of soda has been termed, by Berzelius, *biliary matter*, (gallenstoff) or *biline*; “but the biline of this chemist, and also his sugar of bile, are either pure bile, or choleic acid. Platner has lately obtained the acid choleate of soda in crystals, which is an additional argument in favor of the opinion that bile is a uniform and definite compound of choleic acid, and that the numerous compounds described by Berzelius, and others, as constituents of bile, are *products of the decomposition of choleic acid*. This is a consideration of the utmost importance with reference to the production of bile in the animal body, to its functions, and in short, to chemical physiology.” (GREGORY.)

The components of anhydrous choleic acid, in reference to the formula above quoted, are

|                             |    |      |     |      |        |
|-----------------------------|----|------|-----|------|--------|
| Carbon .....                | 44 | .... | 264 | .... | 65.03  |
| Hydrogen .....              | 40 | .... | 40  | .... | 9.84   |
| Oxygen .....                | 9  | .... | 72  | .... | 17.74  |
| Nitrogen.....               | 1  | .... | 14  | .... | 3.45   |
| Sulphur .....               | 1  | .... | 16  | .... | 3.94   |
| <hr/>                       |    |      |     |      |        |
| Anhydrous choleic acid..... | 1  |      | 406 |      | 100.00 |

#### PRODUCTS OF THE DECOMPOSITION OF CHOLEIC ACID.

1. *Choloidic Acid*. When choleic acid is boiled for several hours with hydrochloric acid, it yields a brownish resin-like substance, which is bitter, fusible, insoluble in water and in ether, but soluble in alcohol, to which Demarçay has given the above name. Ammonia is at the same time formed, and the acid mother-liquor contains a substance termed Taurine.

2. *Taurine* may be obtained directly from bile, by boiling it with hydrochloric acid till the liquor, at first turbid, becomes clear, separating the choloidic acid by decantation, and evaporating till the greater part of the chloride of sodium has separated: 5 or 6 parts of alcohol are then added to the mother-liquor, when the taurine is gradually deposited in acicular crystals, which may be purified by washing them with alcohol, solution in boiling water, and recrystallization. Pure taurine forms colorless 4-sided prisms, which are inodorous and nearly tasteless, neutral, permanent in the air, very soluble in water, but insoluble in absolute alcohol. The formula of taurine is said to be  $C_4 H_7 O_6 N S_2$ . The presence of a very large amount of sulphur in taurine (and in bile) was first announced by Redtenbacher; the discovery is very important in reference to chemical physiology, and the functions of the liver. According to Von Gorup Besang, when bile is left to itself, the mucus acts as a ferment, and it undergoes a species of fermentation or decomposition, the products of which are the same as those formed when bile is boiled with certain acids; namely, choloidic acid, taurine, and ammonia: he recommends this as a good mode of obtaining taurine.

3. *Cholic Acid*. When bile, or choleic acid, is boiled in a silver vessel with a concentrated solution of caustic potassa till ammonia ceases to be evolved, and water occasionally added to prevent evaporation to dryness, a dark-colored soft mass is formed; this is to be removed from the alkaline liquor, dissolved in water, excess of acetic acid added, and the whole agitated with thrice its volume of ether; the ethereal solution,

when poured off and left to spontaneous evaporation, deposits crystallized cholic acid: it is scarcely soluble in water, but readily soluble in alcohol and ether: it has an acid reaction, a bitter taste, and forms soluble salts with the alkalis. "Schlieper has shown that choleic acid is converted by the action of nitric acid into products, the chief of which is *cholesteric acid*; this fact is important, as, in conjunction with the experiments of Redtenbacher, it establishes a near relation in constitution, between choloidic acid, cholesterine, and cholic acid, all of which, when acted on by nitric acid, yield cholesteric acid." (*Turner's Chemistry*, p 1298.)

A variety of other products have been described as derivatives from bile, but they have not been adequately defined or examined, nor are the extant analyses of the preceding acids to be relied on. Some of them appear to be the preceding substances in an impure state, or mixtures of them; such are *dyslysine*, *fellic acid*, *fellinic acid*, &c.

**BILIARY CALCULI. GALL-STONES.** These concretions have been especially examined by Gren, Thenard, Fourcroy, and, as to the fatty matter which they contain, by Chevreul. (*Ann. de Chim.*, xcv. 5.) Human gall-stones are, for the most part, composed of a crystalline substance, termed by Chevreul *cholesterine* (from *χολη*, *bile*, and *στερεος*, *solid*), with more or less coloring-matter, muco-albumine, and inspissated bile; they are accordingly of various colors and textures, but generally brittle and friable. Those which are chiefly cholesterine, are white and crystalline, and lighter than water; the others are more tough, colored, and dense; their specific gravities, therefore, vary from 0.803 to 1.06. Their chemical examination may be conducted as follows: They may be powdered and digested in water to separate the inspissated bile: then boiled in alcohol, and the solution filtered whilst hot; as it cools it deposits the cholesterine, and often retains common fat and its acids in solution. The portion which resists the action of alcohol may be digested in a weak solution of caustic potassa, which takes up coloring matter and muco-albumine; the solution, supersaturated by acetic acid, deposits these, and the coloring matter may afterwards be removed by alcohol.

*The gall-stones of the ox* frequently consist chiefly of the yellow coloring-matter of the bile, which is occasionally used by painters, on account of its brightness and durability: it is insoluble in water and alcohol, but readily soluble in weak solution of potassa, from which it is thrown down in green flocks by hydrochloric acid: nitric acid, cautiously dropped into a solution of this coloring-matter, gives it various shades of green, blue, and red.

*A gall-stone from a sow* yielded cholesterine 6.0, resin 45, soda with resin 3.6, mucus, coloring matter, phosphate of lime, and oxide of iron, 45.4. (LASSAIGNE.)

**CHOLESTERINE**,  $C_{36}H_{72}O$ , which constitutes the bulk of the above-mentioned gall-stones, has been found in some morbid secretions; it has also been detected in the brain, and in yolk of egg: it is best obtained pure, from the crystalline gall-stones, by boiling them, first in water, and then in alcohol: the boiling alcoholic solution deposits it on cooling, and it then only requires washing with cold alcohol and drying.



Cholesterine forms white pearly flakes, lighter than water, and fusible at  $293^{\circ}$  into a colorless fluid, which does not concrete till cooled to  $240^{\circ}$ , when it assumes the form of a radiated translucent friable mass. It is insoluble in water, and scarcely soluble in cold alcohol; it dissolves in boiling alcohol, and wood-spirit, and in oils. In close vessels it may be sublimed unchanged. According to Wagner, 4 parts of soap in water dissolves 1 part of cholesterine. It is not acted upon by the alkalis even when long boiled in their solutions.

Cholesterine has been analysed by Chevreul, Couerbe, and Marchand, with the following results:

|              |    |     |     |     |        | Chevreul. |         | Couerbe. |        | Marchand. |        |
|--------------|----|-----|-----|-----|--------|-----------|---------|----------|--------|-----------|--------|
| Carbon.....  | 36 | ... | 216 | ... | 85.04  | ...       | 85.095  | ...      | 84.89  | ...       | 84.90  |
| Hydrogen     | 30 | ... | 30  | ... | 11.81  | ...       | 11.880  | ...      | 12.09  | ...       | 12.00  |
| Oxygen ....  | 1  | ... | 8   | ... | 3.15   | ...       | 3.025   | ...      | 3.02   | ...       | 3.10   |
| Cholesterine | 1  |     | 254 |     | 100.00 |           | 100.000 |          | 100.00 |           | 100.00 |

*Cholesteric Acid. Nitrocholesteric Acid.* This compound is produced by long boiling cholesterine in nitric acid; it forms yellow acicular crystals, of a butyraceous odor, little soluble in water, but readily soluble in alcohol and ether. It fuses at about  $138^{\circ}$ , but cannot be sublimed without decomposition. The compounds which it forms with the alkalis are soluble, but those with the other bases are mostly insoluble. The formula assigned to it, deduced from Pelletier's analysis, is  $C_{26}H_{20}O_2N$ .

INTESTINAL CONCRETIONS sometimes bear a resemblance to gall-stones, but they often contain peculiar substances, or are formed upon extraneous nuclei. Dr. Ure has described one resembling ambergris. (*Dict., Art. Intestinal Concretions.*) One examined by Children (*Phil. Trans.*, 1822) consisted of animal matter, chiefly gelatine, 25.20; resin 3.90; ammonio-magnesian phosphate 5.16; phosphate of lime 45.34; vegetable fibre 20.30. These concretions are not uncommonly formed upon fruit-stones, and seem to be peculiarly frequent where the diet has consisted of oatmeal.

Alvine calculi have sometimes a peculiar softness upon the surface, resembling velvet. One of these was found by Dr. Wollaston to consist of extremely minute vegetable fibres, or short needles, pointed at both ends, which he immediately conjectured to arise from some kind of food. For some time, however, he failed in his attempts to trace this substance to its origin; but Mr. Clift, of the College of Surgeons, to whom the subject was mentioned, having put the question whether this fibrous substance might not proceed from *oats*, Dr. Wollaston was induced to examine the structure of this seed; and the result fully verified the conjecture. In Dr. ALEXANDER MONRO'S *Morbid Anatomy of the Gullet*, mention is made of 42 alvine concretions collected by the author's father, which were examined by Dr. Thomson. Their structure (with one exception, similar in all) is described by Dr. Monro "as more or less porous, and somewhat like a dried sponge, and when examined by the aid of a magnifying glass, seems to be made up of a number of very small fibres intimately interwoven with each other, like those in a hat, or in chamois leather; and the interstices between the fibres are filled up with earthy matter." And he adds, "in the centre of the concretion, a *prune*, or a *cherry-stone*, or a small piece of bone, or a biliary calculus, is generally found."

Under the name of *lithofellic acid* Göbel has described a substance which he obtained from a nondescript calculus, which however was probably one of those concretions termed *Bezoar-stones*. In 1844 T. Taylor made the curious discovery of the identity of the substance constituting the so-called *Oriental Bezoars*, which appear to be the *intestinal concretions* of a species of antelope, with *Ellagic acid*. (p. 1292). (*Phil. Mag.*, Dec. 1845.)

AMBERGRIS, which is a concretion from the intestines of the spermaceti whale, contains a considerable portion of a fat-like matter, amounting, in some specimens, to 60 *per cent.*, which, according to Chevreul, resembles cholesterine. Pelletier and Caventou (*Journ. de Pharm.*, vi. 40) have given it the name of *Ambreine*: it may be represented by the formula  $C_{36}H_{32}O$ : it is stated to be convertible by nitric acid into a peculiar body, which they have called *ambreic acid*. It is only found in the unhealthy animal. (HOME'S *Lectures on Comparative Anatomy*, vol. i. p. 740.) Benzoic acid has been found in some specimens of ambergris; in others, equally genuine, there are no traces of it.

*Musk*, *castor*, and *civet*, exclusive of their peculiar and odorous principles, contain distinct species of fat. Musk has been analysed by Blondeau and Guibourt, (*Journ. de Pharm.*, vi. 105,) and by Geiger and Reinmann (*Gmelin's Handbuch*); but its odorous principle has not been isolated. (See also PEREIRA. *Mat. Med.*, Art. *Musk*.)

CERUMEN, or the waxy secretion which lines the external tube of the ear, has been examined by Fourcroy and Vauquelin, (*Fourcroy's Système des Conn. Chymiques*, v., 274,) and more in detail by Berzelius. (*Thier-Chemie: Lehrbuch*, iv.) According to Vauquelin, it contains 0.625 of a brown buttery oil, soluble in alcohol, 0.375 of an albuminoid substance, and a bitter principle. According to Berzelius it is a compound of a soft fat, with albumine, and another peculiar principle, a yellow bitter extract soluble in alcohol; it also contains alkaline and calcareous lactates, but no chloride, and no soluble phosphate.

BRAIN. According to Vauquelin (*Annales de Chimie*, LXXXI. 37), the *cerebral substance* consists of water 80.00, white fatty matter 4.53, red fatty matter 0.70, albumine 7.00, osmazome 1.12, phosphorus 1.50, acids, salts, and sulphur 5.15. According to Couerbe (*Ann. Ch. et Ph.*, LVI. 160), there are five distinct fatty matters in the brain, one of which is cholesterine. He considers the proportion of *phosphorus* in the brain of persons of sound intellect to amount to from 2 to 2.5 *per cent.*, but he asserts that this element is in deficiency in the brain of idiots, and in excess in that of maniacs; amounting in the former to not more than 1 to 1.5 *per cent.*, but in the latter to as much as 3, 4, and even 4.5 *per cent.* But this statement is far from probability, and has not been verified. According to Fremy (*Journ. de Pharm.*, XXVII. 453), brain contains a peculiar fatty acid, of which nitrogen and phosphorus are components, and which he terms *cerebric acid*, together with another phosphorized fatty acid, the *oleophosphoric acid*; it also contains cholesterine, oleine, and margarine. The grey portions of the brain appear to be chiefly albuminous, while the fatty matters chiefly abound in the white por-



tions. The characteristic fat-acids of the brain have also been detected in the substance of the liver, and are probably present in the blood.

The substance of the *nerves* seems to be identical, or nearly so, with that of the brain.

A large *concretion*, weighing 54 grammes, of the size of a hen's egg, found in the right ventricle of the brain of an old horse, consisted of cholesterine 58, membrane and albuminous matter 39·5, subphosphate of lime 2·5. It produced no observable symptoms. (LASSAIGNE, *Ann. Ch. et Ph.*, LXii. 222.)

**EGGS.** The albumine of the egg has been already described (p. 1219). The *yolk* of the hen's egg contains about 30 *per cent.* of oil. When the yolk is digested in alcohol a yellow solution is obtained, which deposits a crystalline fat, and leaves, on evaporation, a yellow viscid oil, which easily becomes rancid. (PLANCHE. *Journ. de Pharm.*, ix. 2.) The insoluble residue is white and pulverulent, and consists chiefly of albumine, but contains a considerable portion of phosphorus in some peculiar state of combination.

The changes which the egg undergoes during incubation, have been investigated by Dr. Prout. (*Phil. Trans.*, 1822.) New-laid eggs are somewhat heavier than water, but gradually become lighter by the evaporation of water and substitution of air, through the shell. When an ordinary sized egg is boiled in water it loses about three-tenths of a grain, consisting of the sulphates, phosphates, and carbonates of lime and magnesia, animal matter, and free alkali. Of an egg which weighs 1000 grains, 106·9 parts constitute the *shell*, 604·2 the *white*, and 288·9 the *yolk*. The shell contains about 2 *per cent.* of animal matter, 1 of phosphate of lime and magnesia, and the residue is carbonate of lime with a trace of carbonate of magnesia. The phosphorus contained in the yolk yields the phosphoric acid requisite for the bones of the chick, but the source of the lime for that purpose is not obvious: Dr. Prout could not detect it in the soft parts of the egg, and there is no apparent vascular connexion between the chick and the shell.

*The eggs or roe of fish* contain also a considerable proportion of oil. The roe of the sturgeon, which, when salted, is known under the name of *caviar*, contains 6·2 albumine; 4·3 fat; 24·3 coagulated albumine and membrane; 6·7 common salt; 0·5 phosphate of lime and oxide of iron; 0·58 water. (JOHN.) The *melt*, or *soft roe* of the male fish, resembles in composition the liver or the brain; it yields an emulsion with water, containing fat and albumine, and, when incinerated, much phosphoric acid is found in the coal. The liver of many fish is abundant in a peculiar kind of oil; that of the *cod-fish* yields it in considerable quantity. (p. 1269.)

#### § IV. SALIVA. PANCREATIC JUICE. GASTRIC JUICE. LYMPH. MUCUS. TEARS. HUMOURS OF THE EYE. SYNOVIA. LIQUOR AMNII. PUS.

SALIVA has been examined by Berzelius, (*Lehrbuch*, and *Ann. de Chim.*, LXXXviii. 123,) and more in detail by Tiedemann and Gmelin. (*Ueber die Verdauung*, and *Ann. Ch. et Ph.*, xxv. 266.) The principal use of this secretion appears to be to attenuate, and mix with the food during mastication; it is consequently secreted in great abundance during

a meal; at other times, only in such quantity as to lubricate the mouth and parts adjacent. It has the property of entangling a large quantity of air, which, swallowed with the food, is probably essential to digestion.

*Human saliva* is transparent, viscid, and contains an animal matter frequently termed *mucus*, but its peculiarities have been pointed out by Berzelius, who designates it *salivary matter* (*Speichelstoff*, *Ptyaline*). Under the term *mucilaginous extractive*, a similar principle has been found in other animal fluids. The specific gravity of human saliva fluctuates between 1·0038 and 1·0088. It is generally slightly alkaline; sometimes neutral; and in some diseases (intermittent fever and abscess) sour. According to Thomson it is most commonly very slightly acid; Tiedemann and Gmelin, and Donné (*Journ. de Pharm.*, 3ème Sér., i. 395) found it always alkaline. According to Boudet, the mucus of the mouth is alkaline, but that of the gums acid. (*Ibid.*, p. 396.) There seems little doubt that the composition of saliva, as obtained in the usual way, is liable to vary, for the accounts of the action of precipitants upon it are much at variance, and the statements of Berzelius do not agree with those of Tiedemann and Gmelin. Whatever may be the nature or peculiarities of the animal matter held in solution in saliva, its quantity is small, for on evaporation it leaves not more than from 0·9 to 1·1 *per cent.* of solid residue. Treviranus found that the saliva reddened the persalts of iron, a property ascribed to the presence of a *sulphocyanide*; but this again is an uncertain result, and has been by some ascribed to smoking tobacco. If, as Mitscherlich asserts, (*Poggend. Ann.*, xxviii. 320,) the saliva is alkaline during a meal, but acid at other times, its variable effects upon precipitants is easily accounted for.

The latest experiments upon human saliva are those of Enderlin, (*Ann. der Pharm.*, xlix. 333,) according to whom the alkaline reaction of saliva depends upon the presence of tribasic phosphate of soda: the ashes of saliva afforded him

|  |         |
|--|---------|
| Phosphate of soda [ $3\text{Na O, PO}_5$ ] .....   | 28·122  |
| Chloride of sodium and chloride of potassium ..... | 61·930  |
| Sulphate of soda.....                              | 2·315   |
| Phosphate of lime .....                            | } ..... |
| „        magnesia ....                             |         |
| „        iron .....                                |         |
|  | 97·876  |

According to Berzelius the components of human saliva are

|  |       |
|--|-------|
| Ptyaline .....                         | 2·9   |
| Mucus .....                            | 1·4   |
| Extractive, and alkaline lactates..... | 0·9   |
| Chloride of sodium .....               | 1·7   |
| Soda .....                             | 0·2   |
| Water .....                            | 992·9 |
|  | 100·0 |

According to Gmelin, the saliva of a tobacco-smoker is alkaline; its sp. gr. 1·0043. It leaves, on evaporation, from 1·14 to 1·19 *per cent.* of solid matter, which, when burned, gives 0·25 of ash, of which 0·203 is soluble, and 0·047 insoluble in water. 100 parts of the residue of the evaporation of saliva he found to contain the following substances:



|  |              |
|--|--------------|
| 1. Soluble in alcohol and in water : phosphorised fatty matter, extractive, chloride of potassium, lactate of potassa, sulphocyanide of potassium..... | 31.25        |
| 2. Deposit from boiling alcoholic solution on cooling : animal matter, much phosphate, and a little sulphate of alkali, and chloride of potassium..... | 1.25         |
| 3. Soluble in water only: ptyaline, much phosphate, and a little alkaline sulphate; chloride of potassium .....  | 20.00        |
| 4. Insoluble both in water and in alcohol : mucus, albumine, carbonates, and phosphates.....   | 40.00        |
| Loss .....   | 7.50         |
|  | <hr/> 100.00 |

In the saliva of a person suffering under diseased lungs, whose perspiration smelt sour, and whose gastric juice contained much acetic acid, whilst the urine was highly alkaline, Dr. Prout found free acetic acid. (*Phil. Mag. and Ann.*, iv. 122.) During mercurial salivation, the specific gravity of the saliva was 1.0038, and contained albuminous flakes 0.257, mucus 0.367, chloride of sodium 0.090, water 99.286. (*Thomson's Annals*, vi. 397.) In a similar case, in which the saliva amounted to two quarts daily, Dr. Bostock found it of a pale yellow color and opaque; it deposited, in the course of twenty-four hours, viscid films, and became transparent; it became turbid at 212°, and with hydrochloric acid and corrosive sublimate it gave an albuminous precipitate: it left, on evaporation, 2 per cent. of dry residue. (*Med. Chir. Trans.*, xiii. 73.)

The saliva of the *dog* and of the *sheep* have been analyzed by Gmelin, and that of the *horse*, by Lassaigne. (*Ann. Ch. et Ph.*, xix. 176.) The saliva of the *sheep* contained so much carbonate of soda as to effervesce with acids, and also sulphocyanide of potassium; its solid matter amounted to 1.2 per cent. That of the *dog* left 2.51 per cent. of solid matter, but yielded only very slight traces of sulphocyanogen. The saliva of the *horse* afforded 3.5 per cent. of solid residue, and deposited carbonate and phosphate of lime. According to Schultz and Simon the saliva of the horse contains a notable quantity of *caseine*. Simon found it composed as follows :

|  |              |
|--|--------------|
| Water .....                                | 982.0        |
| Fatty matter, including cholesterine ..... | 0.1          |
| Ptyaline and extractive matter .....       | 4.4          |
| Caseine .....                              | 5.4          |
| Albumine .....                             | 0.6          |
| Extractive matter and salts.....           | 7.2          |
| Loss .....                                 | 3            |
|  | <hr/> 1000.0 |

*Salivary Concretions.* These are sometimes found in the salivary ducts and glands: they have been repeatedly analyzed, and consist chiefly of phosphate of lime, carbonate of lime, carbonate of magnesia, and animal matter. A calculus from the salivary duct of a woman, sixty years of age, was white, friable, specific gravity = 2.30. It contained animal matter 25, phosphate of lime 55, carbonate of lime 15, carbonate of magnesia 1, oxide of iron 2? loss 2. (Bosson.) A calculus from the salivary gland of an ass, contained 91.6 carbonate of lime, 4.8 phosphate of lime, and 3.6 animal matter. (CAVENTOU.) A salivary stone from a horse consisted of, 85.52 carbonate of lime, 7.56 carbonate of magnesia, 4.40 phos-

phate of lime, and 2·48 of animal matter. (HENRY, jun.) Two salivary concretions from a horse, analysed by Wurzer (*Archiv. der Pharm.*, xiv. 254), were composed as follows:

|                                   |        |       |       |
|-----------------------------------|--------|-------|-------|
| Carbonate of lime .....           | 80·50  | ..... | 87·5  |
| Phosphate of lime .....           | 2·75   | ..... | 3·5   |
| Soluble animal matters .....      | 8·60   | ..... | 7·0   |
| Insoluble animal matters .....    | 4·40   |       |       |
| Oxides of iron and manganese..... | 1·00   |       |       |
| Chloride of sodium .....          | 1·00   | ..... | 0·5   |
| Carbonate of soda .....           | 1·75   | ..... | 0·9   |
|                                   | <hr/>  |       | <hr/> |
|                                   | 100·00 |       | 99·4  |

*Tartar of the Teeth.* This term is applied to a deposit formed upon those parts of the teeth which are protected from the cleansing influence of the tongue, and is most abundant in the mouths of persons who speak much, and keep the mouth open, so as to allow of the evaporation of the saliva. It consists of animal matter and earthy phosphates. Berzelius obtained from 100 parts of this substance, ptyaline 1·0, mucus, 12·5, earthy phosphates 79·0, animal matter soluble in hydrochloric acid 7·5. Vauquelin and Laugier obtained 0·13 mucus, 0·66 earthy phosphates, 0·09 carbonate of lime, 0·05 soluble animal matter, 0·07 water. Thomson found phosphate of lime 65·61; carbonate of lime 7·18; silica, with traces of iron and magnesia 1·32; fixed alkaline chlorides 1·43; mucus, albumen, and soluble animal matter 16·51; ptyaline 1·32; water 6·63.

**PANCREATIC JUICE.** This secretion, from a *dog*, contains, according to Gmelin, albumine, and a substance like curd, a small quantity of mucus and osmazome, (salivary matter?) and a free acid. Its salts resemble those of saliva, excepting sulphocyanides. It afforded 91·72 *per cent.* of water. That from the *sheep* contained 1·51 substances soluble in alcohol, 0·28 soluble in water, 2·24 coagulated albumine, 96·35 water. According to Leuret and Lassaigne, (*Journ. de Chim. Medic.*, i. 549,) and Bouchardat and Sandras, (*Comptes Rendus*, xx. 1085,) the pancreatic liquor is always alkaline. The former chemists found the pancreatic liquor of the horse of the same composition as human saliva. It is probable that this secretion contains an azotized principle resembling diastase, for that from a hen rapidly changed starch into dextrine and sugar. According to Bernard and Barreswill the pancreatic juice closely resembles saliva, but is richer in animal matter; when acid, it possesses the properties of gastric juice, but is more powerful. (DUMAS. *Chim. app. aux Arts*, viii. 605.)

**GASTRIC JUICE.** The extraordinary solvent powers of this secretion, and its property of coagulating milk (and other caseous and albuminous liquids?) have been long known, but its chemical nature does not satisfactorily explain these properties. We are indebted to Dr. Prout for the discovery of the presence of hydrochloric acid in this secretion; (*Phil. Trans.*, 1824;) he found it, together with acetic acid, (lactic acid?) in the gastric juice of the rabbit, hare, horse, calf, and dog, and in the sour matter thrown up by persons suffering from indigestion. According to Tiedemann and Gmelin, any foreign matter in the stomach excites this acid secretion, but especially stimulating food. Blondlot referred the



acidity of the gastric juice to the presence of an acid phosphate of lime, but Melsens found it to act upon fragments of crystallized carbonate of lime, showing that the acid is in a free state. (*Comptes Rendus*, xix. 1289.) Tiedemann and Gmelin found acetic and butyric acid in the gastric juice of a horse. According to Bernard and Barreswill, the free acid is the phosphoric. (*Ibid.*, p. 1284.)

**LYMPH.** This term is applied to the fluid which lubricates the different cavities of the body, and which moistens its cellular textures; it sometimes collects in morbid quantity, as in *dropsies*; it is found in the thoracic duct of an animal that has been kept for twenty-four hours without food. The liquid of vesications also seems, chemically speaking, closely to resemble it. It is colorless, transparent, miscible in all proportions with water, does not affect vegetable blues, and is not coagulated by acids or by alcohol, but when evaporated to dryness it yields slight traces of albuminous matter. Several liquids have been examined under the name of *lymph*, from wounds, and other sources, but the results, as might be expected, are very discrepant. Its properties, in dropsical cases, are liable to much variation, depending probably upon the cause of its accumulation, and the manner in which it has been thrown out. When this has been a very gradual process, its characters are those of common lymph; but when rapid, or attended by inflammatory action, it is more abundant in albumine, and sometimes approaches *serum* in its characters and composition; hence dropsical fluids are often very dissimilarly constituted, as far, at least, as regards quantitative composition.

**MUCUS.** All animal fluids of a viscid or glairy consistence, and not partaking of the decided characters of albumine, were formerly classed under this term, till Hatchett, in his valuable essays on animal substances, and especially in his observations on the component parts of membrane, showed the necessity of assigning to it a more definite meaning. Bostock includes, under the term *mucus*, animal substances which are soluble in hot and cold water; not precipitated by tannine or corrosive sublimate; not gelatinizable; but which are thrown down by subacetate of lead. Fourcroy and Vauquelin improperly compare it to gum. Berzelius remarks, that if the term *mucus* be restricted to the secretion from what are termed *mucous membranes*, it will include a variety of dissimilar products. In a paper already quoted, I have shown that the characters generally ascribed to mucus, are in some cases derived from peculiar forms or combinations of albumine.

The secretion which is most appropriately termed *mucus*, is that from the nasal membrane; its properties are amply given by Berzelius. It appears when first secreted to be thin and aqueous, but, subject from its situation to the constant action of air, and to evaporation, it gradually thickens. It contains *mucus* (a peculiar animal principle) 5·33; extractive matter soluble in alcohol, and an alkaline lactate 0·30; chlorides of potassium and sodium 0·56; extractive matter, soluble in water only, with traces of albumine and a phosphate, 0·35; soda combined with the mucus 0·09; water 93·37. Of these components, the *mucus* is the only one which is peculiar to this secretion; its properties are defined by Berzelius as follows: it swells and acquires apparent fluidity in water,

without being actually dissolved, but gives a ropiness to it when present to a less amount than 1 per cent. With pure water of the temperature of  $95^{\circ}$  this appearance ensues in a few hours, but if the apparent solution be filtered, the mucus remains upon the paper and gradually thickens; it may be repeatedly dried and moistened without material change of properties; it, however, becomes less transparent, yellow, and at length has a purulent appearance. When boiled in water it does not harden and shrink, but becomes tough, and on cooling is found to retain its former characters. When dried, it is yellow and translucent. Subjected to destructive distillation, it yields carbonate of ammonia and empyreumatic oil; and phosphate and carbonate of lime, and a trace of carbonate of soda, are found in the residuary ash. It is soluble in dilute sulphuric acid, and is blackened and decomposed by the concentrated acid. Dilute nitric acid coagulates, and tinges it superficially yellow, after which it swells and becomes viscid as at first: when digested in the acid it is entirely dissolved. Acetic acid coagulates, but does not dissolve it; it, however, acquires a trace of albumine, and consequently becomes cloudy on the addition of ferrocyanide of potassium. Caustic potassa first renders it more viscid, and then dissolves it. Infusion of galls thickens and coagulates it in all its states.

In *Oysters*, in the *vertebral fluid* of the *Squalus maximus*, and in *frog-spawn*, are contained modifications of *mucus*; that of *frog-spawn* is very remarkable from the extent to which it swells up in water, forming a very bulky and transparent jelly; so that a piece not larger than a pea of the recently-emitted gelatinous matter that envelops the ova of the frog, will gradually absorb and gelatinize 8 or 10 ounces of water.

The *mucus of the urinary bladder* (together with that of some dropsical fluids,) has been examined by Caventou. (*Ann. Ch. et Phys.*, 3ème Sér., viii. 321.)

TEARS contain a small portion of albumine combined with soda, chloride of sodium, and water. There are also small portions of other salts.

HUMORS OF THE EYE. The *aqueous* and *vitreous humors* are composed of water holding a minute quantity of albumine and saline matter in solution; the *crystalline lens* also contains more than half its weight of water, the remainder being an albuminous substance, with traces of chlorides.

SYNOVIA is the fluid which lubricates the surfaces of joints. It contains, according to Hatchett (*Phil. Trans.*, 1799,) a small portion of phosphate of lime, and of phosphate of soda and ammonia; the animal principle appeared to be albumine.

LIQUORS OF THE AMNIOS AND ALLANTOIS. The human *liquor amnii* is alkaline and albuminous; it yields copious precipitates with corrosive sublimate and infusion of galls. It is also said to contain benzoic acid and urea. Soda, chloride of sodium, and phosphate and carbonate of lime, are its principal saline ingredients; and Prout found traces of sugar of milk in it. (*Ann. of Phil.*, v. 417.) The solid contents amount to between 2 and 3 per cent. The acid described by Buniva and Vauquelin (*Annales de Chimie*, xxxiii. 270,) as peculiar to the *liquor amnii* of the cow, and termed *amniotic acid*, was found by Dzondi



to belong to the liquor of allantois, or to the urine of the foetus. The *allantoic acid* is obtained by evaporating the allantoic liquid of the foetal calf: it forms white acicular crystals, sparingly soluble in water, but yielding soluble salts with the alkalis. It has been produced artificially by Liebig, by the action of peroxide of lead on *uric acid*. The liquor of the amnios has also been examined by Bostock (*Schweigger's Journ.*, xxiii. 407); by Frommherz and Gugert (*ibid.*, l. 191); by Rees (*Phil. Mag.*, 3rd Ser., xiii. 395); and by Lassaigne (*Ann. Ch. et Ph.*, xxii. 300.)

**PUS.** This, and the term *purulent matter*, is applied to the secretion of inflamed and ulcerated surfaces, and its characters are very different according to the circumstances under which it is secreted. When it indicates a healing sore, it has been called *healthy pus*, and has the following properties. It has the consistency of cream, a yellowish color, and exhibits, under the microscope, the appearance of globules diffused through a fluid. (HOME, *On Ulcers*, 2nd edit., p. 13.) Its specific gravity is about 1.030. It does not affect vegetable colors till it has been some time exposed to air, when it becomes slightly sour; it does not easily mix with water, alcohol, or dilute acids. (PEARSON, *On Pus*, *Nicholson's Journal*, xxx.) The composition of pus has not been accurately determined, and there is no accurate test by which it can be satisfactorily distinguished from albuminous and mucous secretions, when, as is almost always the case, it is more or less mixed with those animal fluids.

The *matter* expectorated in *phthisis* has been examined by Caventou. (*Ann. Ch. et Ph.*, Juillet, 1843.) He found water 850, chloride of sodium 10, soda 3, animal matter and phosphate of lime 137, in 1,000. He also examined three specimens of *pus*; it formed with hydrochloric acid a viscid solution, which became limpid and almost transparent, and afterwards blue. With caustic potassa it formed a glairy mixture, which was decomposed by excess of hydrochloric acid; the substance which at first separated redissolved, and the solution became blue. When pus is acted on by sulphuric, nitric, or hydrochloric acid, it exhales a peculiar smell resembling that of glue: its alkaline solution also exhales a nauseous odor.

## § V. URINE. UREA. URIC ACID. URINARY CALCULI.

**URINE.** This secretion carries off several substances from the blood, which may be termed excrementitious, and which would be injurious if retained; these substances are, for the most part, abundant in nitrogen. The *quantity* of urine which is formed, or secreted, in the ordinary and healthy state of the system, is very variable, depending upon the quantity of liquids taken into the stomach, the extent of perspiration, the state of the nervous system, and apparently in many cases, upon the dry or humid state of the atmosphere, a cause by which the abstraction of moisture by the skin is greatly modified. Between 30 and 40 ounces may, perhaps, be considered as the average quantity of the urine voided by a healthy person, living upon ordinary diet, in the course of each 24 hours.

But the *quality* of the urine is no less variable than its quantity, so that its density is perpetually varying; sometimes its specific gravity scarcely exceeds that of water; at others, it rises to 1.030, or even in

some diseased states, to 1·040; that which is voided in the morning by a healthy person who has eaten and drunk moderately of ordinary diet, is generally about 1·020: its usual range being between 1·015 and 1·030. It is limpid, and of various tints of yellow. Its taste is saline and bitterish. Its solid contents may be estimated at between 7 and 8 *per cent.*

Recent healthy urine almost always has more or less of an acid reaction upon tests; after it has stood in an open vessel for a few hours, this acidity gradually becomes less apparent, and it generally deposits a little mucus, containing traces of acid urate of ammonia. It is extremely prone to other and more complicated changes, and in warm weather it begins in the course of a few hours to acquire new properties: it becomes alkaline, acquires a highly disagreeable odor, and lets fall a whitish sediment, consisting chiefly of ammonio-magnesian phosphate, and phosphate of lime; it afterwards smells ammoniacal, and is found to hold carbonate of ammonia in solution. Similar changes may be effected by continued boiling; they are chiefly referable to the decomposition of the characteristic ingredient of the urine, namely *urea*, a substance which is easily resolved into carbonate of ammonia.

The term *urinary fermentation* has been applied to the spontaneous changes which urine undergoes, and which terminate in this decomposition of the urea. According to the experiments of Jacquemart, (*Ann. Ch. et Ph.*, 3ème Sér., Feb. 1843,) healthy urine, in a perfectly clean vessel, changes but slowly, and requires as much as 14 days for its entire putrefaction (at medium temperature?) The addition of 1 *per cent.* of yeast to the same urine, accelerates the process, and it is then completed in about 7 days; but if about 8 *per cent.* of urine already putrid be added to it, the changes are then completed in 3 days. It would appear that in healthy urine, the mucus passes into the state of a ferment by the action of the air. The most powerful agent for inducing the putrefaction of urine is the white sediment deposited in urinals; 2 parts of it added to 100 of fresh urine, completes the change in 24 hours. When fresh and healthy urine is preserved in a clean phial, and air cautiously excluded, it remains transparent, retains its acidity, and undergoes scarcely any apparent change beyond that of occasionally depositing a little uric acid.

The following substances are always found in healthy urine:—

- |   |                           |
|---|---------------------------|
| 1. Water.                                       | 6. Phosphate of ammonia.  |
| 2. Carbonic acid.                               | 7. Phosphate of soda.     |
| 3. Phosphoric acid, or super-phosphate of lime. | 8. Phosphate of magnesia. |
| 4. Uric acid, or superurate of ammonia.         | 9. Common salt.           |
| 5. Phosphate of lime.                           | 10. Sulphate of soda.     |
|   | 11. Albumine.             |
|   | 12. Urea.                 |

To which some have added,

- |                                     |                                  |
|-------------------------------------|----------------------------------|
| 13. Fluoric acid.                   | 19. Fluoride of calcium.         |
| 14. Benzoic acid.                   | 20. Hydrochlorate of ammonia.    |
| 15. Acetic or lactic acid.          | 21. Sulphur.                     |
| 16. Gelatine.                       | 22. Silica.                      |
| 17. Lactate, or acetate of ammonia. | 23. Mucus.                       |
| 18. Sulphate of potassa.            | 24. Coloring and odorous matter. |



To this extensive list may be added a variety of occasional or accidental ingredients derived from particular kinds of food or medicine, and which pass off by the kidneys; and lastly, certain substances which are apparently products of disease, such as oxalic acid or oxalate of lime, carbonate of lime, cystic oxide, sugar, and nitric acid.

From this complicated character of the urine, from the variations to which the quantity and quality of its components are liable, and from the facility with which it passes into a state of decomposition, and is modified by heat and other chemical agents, it becomes extremely difficult to give even an average statement of the relative proportions of its usual ingredients; as a specimen, however, of such an attempt, I quote the following from Berzelius:—

|   |               |
|---|---------------|
| Water .....   | 933·00        |
| Urea .....  | 30·10         |
| Sulphate of potassa.....                              | 3·71          |
| Sulphate of soda.....                                 | 3·16          |
| Phosphate of soda .....                               | 2·94          |
| Chloride of sodium.....                               | 4·45          |
| Phosphate of ammonia .....                            | 1·65          |
| Hydrochlorate of ammonia .....                        | 1·50          |
| Free lactic acid .....                                | } 17·14       |
| Lactate of ammonia .....                              |               |
| Animal matter soluble in alcohol .....                |               |
| Urea not separable from the preceding .....           |               |
| Earthyphosphates, with a trace of fluoride of calcium | 1·00          |
| Uric acid .....                                       | 1·00          |
| Mucus of the bladder.....                             | 0·32          |
| Silica .....  | 0·03          |
|   | <hr/> 1000·00 |

A question has arisen as to the existence of *free* acid in the urine, as stated by Berzelius and others; Dr. Prout regards the acidity of the urine as the result of the presence of acid or super-salts, and especially of superphosphate of lime and superurate of ammonia. Dr. Turner observes, “That a very strong argument, which to him appears conclusive in favor of this view, is, that on adding hydrochloric acid to recent urine, minute crystals of uric acid are gradually deposited, as always happens when this acid subsides slowly from a state of solution; but on the contrary, if no free acid is added, an amorphous sediment, which Dr. Prout regards as superurate of ammonia, is obtained.” We know, however, too little of the mutual actions of the complex ingredients of the urine, to sanction this opinion; carbonic acid is certainly, sometimes at least, present in a free state, and whether other acids may or may not exist free, and therefore in variable quantities in reference to the bases, is a question not at present determined. At all events, the presence of free acid in certain morbid states of the urine, cannot admit of a doubt. One important consequence of the acid state of the urine appears to be the retention of certain difficultly-soluble salts, in permanent solution; for whenever the urine is neutralized by an alkali, these are more or less precipitated; an effect of this kind not unfrequently takes place in the body, as we see from the turbid state in which the urine is voided after sufficient doses of the caustic or carbonated alkalis, or of magnesia.

Berzelius ascribes the acidity of the urine to the presence of free



lactic acid, and according to Cap and Henry, the urea is held in the urine in the state of *lactate*; (*Journ. de Pharm.*, xxvii. 355,) but Gregory, and others, failed in verifying their experiments; and according to Liebig, if lactic acid in any form is ever present, it is an abnormal product, and is not contained in healthy urine, either fresh, or putrid.

Liebig ascribes the acidity of fresh urine to the presence of uric and of hippuric acid, both which acids, he observes, are more soluble in a solution of phosphate of soda, than in water. He also found that putrid urine, when distilled with a fixed acid, yields acetic acid, as originally announced by Proust in 1820. (*Ann. Ch. et Ph.*, xiv. 260.)

Scharling, by the action of ether upon concentrated urine, has separated a brown fusible resin-like substance, which he calls *oxide of omichmyle*, from (*ομυχμα*, urine;) but which, according to Löwig, is probably impure hippuric acid. (*Chem. d. Org. Verbind.*, ii. 700.) He also obtained, by distilling urine with nitric acid, benzoic acid, and an acid containing chlorine, derived from the decomposition of the salts of the urine; he obtained the same acid by distilling oxide of omichmyle with nitrohydrochloric acid, and gives a formula which represents it as benzoic acid, in which 1 atom of hydrogen is replaced by 1 of chlorine. The presence of benzoic acid in urine, originally detected by Proust, may be ascribed to the decomposition of hippuric acid. (See p. 1373.) In 1844 Pettenkofer (*Ann. der Pharm.*, lii. 97,) discovered a substance in urine, capable of forming a crystalline compound with chloride of zinc; this is, according to Liebig, a compound of *kreatinine*, (see *muscular fibre*,) and chloride of zinc; both kreatine and kreatinine have lately been found by Liebig in the urine.

The preceding remarks will show that the chemistry of the urine is still in an imperfect state; that it contains several substances which were long overlooked, and gives rise to the formation of others which have been very imperfectly examined. According to Liebig, *normal urine* may be either *acid*, *neutral*, or *alkaline*, its state depending upon diet and other causes. When the food abounds in salts composed of the alkalis combined with organic acids, the urine becomes alkaline in consequence of the destruction of the organic acid, which in the process of circulation and respiration is converted into carbonic acid, so that alkaline carbonates appear in the urine. In this way an *alkaline* urine is voided after the use of citrate, tartrate, or acetate of potassa or of soda. When the food contains a smaller quantity of such organic salts, the urine may of course be *neutral*; and when they are altogether absent, or, as is generally the case, only contained in very small relative quantities in our food, then *acid* urine will be voided.

According to Liebig, (*Turner's Chemistry*, 8th Ed., p. 1305,) an *artificial urine* may be formed "by dissolving in 1 pound of hot water 40 grains of *dry* phosphate of soda,  $2\text{NaO}, \text{HO}, \text{PO}_5$ ; or 90 grains of the *crystallized* phosphate,  $2\text{NaO}, \text{HO}, \text{PO}_5, + 24\text{HO}$ ; and then dissolving in the alkaline solution thus formed, 15 grains of uric acid, and 15 grains of hippuric acid; on cooling, and after standing for some time, 7·5 grains of uric acid, or of acid urate of soda, are deposited, precisely similar in form and aspect to the uric deposit in urine; 22·5 grains of the organic acids remain dissolved, and the liquor has a strong acid reaction. The addition of an acid causes a precipitate of uric acid, as in real urine."



The properties and composition of the ordinary acids, bases, and salts of the urine, are already before the reader; the chemical history of *urea*, and of *uric acid*, bodies which peculiarly characterise urine, remain to be noticed.

UREA.  $C_2H_4O_2N_2$ . This is the principle which confers upon the urine its chief peculiarities. It was discovered by Rouelle (*Journ. de Médecine*, 1773 et 1777,) and afterwards more fully described by Cruikshanks (*Rollo on Diabetes*. Appendix to 2nd Ed., 1798,) and by Fourcroy and Vauquelin, (*Annales de Chimie*, 1800, xxxi. 48; et xxxii. 80.) It was first obtained pure, and accurately analyzed by Prout, (*Medico-Chirurgical Transactions*, 1818, vol. viii.,) and is the subject of a very interesting series of researches by Wöhler, who discovered its production from cyanic acid and ammonia (*Poggend. Annalen*, xii. 253,) being the first instance of the direct artificial formation of an organic compound.

Urea may be obtained: (1.) *From urine*. Evaporate urine by a gentle heat (never exceeding  $200^\circ$ ), to the consistence of a thin syrup, and whilst still warm, add to it an equal volume of colorless nitric acid, (sp. gr. 1.35,) which should be perfectly free from nitrous acid; a brisk effervescence ensues in consequence of the destruction of the coloring matter, and there is at the same time a copious deposition of crystallized, and nearly pure *nitrate of urea*. The evaporated urine should not be allowed to cool before the acid is added, for in that case the crystals are very brown. The nitrate of urea is dissolved in water, and having been recrystallized, is treated with carbonate of baryta or of potassa, till rendered neutral: on evaporating the clear solution, crystals of nitrate of baryta (or nitrate of potassa,) are first obtained, and then those of urea; the latter are purified by redissolving them in a little cold water, evaporating to dryness, and digesting the residue in alcohol, which takes up the urea, and furnishes it in crystals when evaporated. If the urea is colored, a little permanganate of potassa may be added to its aqueous solution, which has no action on urea, but destroys the coloring matter. Any color communicated by excess of permanganate is instantly destroyed by a few drops of alcohol, and the filtrate then yields colorless crystals of urea. (GREGORY.) (2.) The concentrated urine may be saturated by oxalic acid, which yields crystals of *oxalate of urea*; these, dissolved in water, decolorized by animal charcoal, and decomposed by digestion with carbonate of lime, yield a solution from which colorless crystals of urea may be obtained. (3.) *From cyanate of ammonia*. 28 parts of dried ferrocyanide of potassium, and 14 parts of binoxide of manganese, are mixed in powder, and calcined upon an iron plate heated to dull redness; the mixture takes fire, but is gradually extinguished, and must be stirred, while cooling, to prevent agglutination. The cold mass is then powdered and digested in cold water, which takes up the *cyanate of potassa*; this solution is filtered off and set aside; the remaining powder is then washed with a second portion of cold water and again filtered, and in this filtrate, 20.5 parts of *sulphate of ammonia* are dissolved, and the solution added to the first filtered solution of the cyanate. A large quantity of sulphate of potassa is deposited, which is strained off, and the filtered liquor, now containing, with some sulphate of potassa, all the cyanate of ammonia, is evaporated to dryness, during which process the cyanate of ammonia

is transformed into *urea*. The dry mass is digested in alcohol, which only dissolves the urea, and yields it pure, on evaporation. (LIEBIG, *Annalen der Pharm.*, xxxviii. 108.)

*Urea* crystallizes in flattened four-sided prisms; they generally resemble nitre in appearance, and have a similar cooling saline taste. They are inodorous. Their sp. gr. is 1.35. They are soluble in their own weight of cold water, and in every proportion in hot water; they dissolve in 4.5 of cold, and in 2 parts of boiling alcohol; but they are insoluble in ether. Their solution is neither acid nor alkaline, but urea belongs to the class of *organic bases*, and forms crystallizable compounds with several of the acids.

Pure urea is permanent in the air; at  $250^{\circ}$  it fuses into a colorless liquid; at a higher temperature it yields ammonia, cyanate of ammonia, and dry solid cyanuric acid. Alkalis do not evolve ammonia by their action upon urea, unless aided by heat; but when fused with them, it is resolved into carbonic acid and ammonia. An aqueous solution of urea remains long without change; but the addition of proteiniferous substances resolves it more rapidly into carbonate of ammonia. In this case 1 atom of urea, and 2 atoms of water, yield 2 atoms of carbonate of ammonia.  $\text{C}_2\text{H}_4\text{O}_2\text{N}_2 + 2\text{HO} = 2[\text{NH}_3, \text{CO}_2]$ . When nitrate of silver and a little potassa is added to a cold solution of urea, a compound of oxide of silver with urea is thrown down; but if the mixed solution of urea and silver is evaporated at about  $120^{\circ}$ , nitrate of ammonia and cyanate of silver are the results; an atom of urea containing the elements of an atom of cyanic acid, an atom of ammonia, and an atom of water.  $\text{C}_2\text{H}_4\text{O}_2\text{N}_2 = \text{NC}_2\text{O} + \text{NH}_3 + \text{HO}$ .

The components of urea are,

| The components of urea are, |   |     |    |     |        |        |        |     |        | Liebig<br>and<br>Wöhler. |
|-----------------------------|---|-----|----|-----|--------|--------|--------|-----|--------|--------------------------|
|                             |   |     |    |     |        | Prout. |        |     |        |                          |
| Carbon.....                 | 2 | ... | 12 | ... | 20.00  | ...    | 19.975 | ... | 20.02  |                          |
| Hydrogen .....              | 4 | ... | 4  | ... | 6.67   | ...    | 6.650  | ... | 6.72   |                          |
| Oxygen .....                | 2 | ... | 16 | ... | 26.66  | ...    | 26.650 | ... | 46.72  |                          |
| Nitrogen .....              | 2 | ... | 28 | ... | 46.67  | ...    | 46.650 | ... | 26.54  |                          |
| <hr/>                       |   |     |    |     |        |        |        |     |        | <hr/>                    |
| Urea.....                   | 1 |     | 60 |     | 100.00 |        | 99.925 |     | 100.00 |                          |

Dumas represents urea as an *amide of carbonic oxide*, by the formula,  $2\text{NH}_2 + \text{C}_2\text{O}_2$ .

*Nitrate of Urea.*  $\text{C}_2\text{H}_4\text{O}_2\text{N}_2, \text{NO}_5, \text{HO}$ . When pure nitric acid is added to an aqueous solution of urea, a white granular precipitate falls, which, dissolved in warm water and recrystallized, furnishes large lamellar plates. These crystals are soluble in 8 parts of cold water. Heated above  $212^{\circ}$  nitrate of urea is decomposed, evolving carbonic acid and nitrogen. At  $284^{\circ}$  it is resolved, according to Pelouze, into carbonic acid and nitrous oxide, in the proportion of 2 volumes to 1, and the residue is urea and nitrate of ammonia; at a higher temperature, water, nitrous oxide, carbonic acid, and ammonia are the products.

*Nitrous acid* immediately decomposes urea; equal volumes of carbonic acid and nitrogen are evolved, and nitrate of ammonia is formed.  $\text{C}_2\text{H}_4\text{O}_2\text{N}_2 + 2\text{NO}_4 = 2\text{CO}_2 + \text{N}_2 + \text{NH}_4\text{O}, \text{NO}_5$ .

*Oxalate of Urea.*  $\text{C}_2\text{H}_4\text{O}_2\text{N}_2 + \text{C}_2\text{O}_3 + \text{HO}$ . This salt is thrown down in foliated crystals, on mixing aqueous solutions of oxalic acid and urea: it is less soluble than the nitrate.



*Hydrochlorate of Urea.*  $\text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2, + \text{HCl}$ . Urea absorbs dry hydrochloric gas, forming a yellow liquid, which afterwards concretes into a crystalline mass, having, according to Pelouze, the preceding formula. (*Ann. der Pharm.*, xliv. 102.) This compound is immediately decomposed by water, and resolved into urea and hydrochloric acid; but it is soluble, according to Erdmann, in anhydrous alcohol, without apparent decomposition; but the crystals deposited from this solution are those of sal ammoniac. (*Erdmann and Marchand's Journ.* xxv. 506.)

*Acetate of Urea.*  $\text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2, + \text{C}_4 \text{H}_3 \text{O}_3, + \text{HO}$ . This salt was obtained by Gregory in the form of a mass of prismatic crystals, very soluble in water.

COMPOUNDS OF UREA WITH SALTS. When urea is rubbed with salts containing water of crystallization, the mixture liquifies, but the urea does not appear to combine with the water. Werther (*Erdmann and Marchand's Journ.*, xxxv. 51) has formed combinations of urea with salts, but they appear to have feeble affinities. The urea has been represented as performing the part of water of crystallization, but the compounds are not decomposed by water; so that the affinity of urea for the salt exceeds that of water. It has also been assumed that the urea forms a *coupled acid* by combining with the acid of the salt, which then unites to the bases. (LÖWIG.)

*Urea and Chloride of Ammonium.*  $\text{NH}_4 \text{Cl}, + \text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2, + 2\text{HO}$ , formed by evaporating a solution of 1 atom of sal ammoniac with 1 of urea, yields moderately large crystals.

*Urea and Chloride of Sodium,*  $\text{NaCl}, + \text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2, + 2\text{HO}$ , crystallizes in shining rhombic prisms, very soluble in water. They are partially decomposed by absolute alcohol, and chloride of sodium separates. Nitric acid added to their aqueous solution throws down nitrate of urea.

*Urea and Chloride of Mercury.*  $2\text{HgCl}, + \text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2$ . When a hot alcoholic solution of urea is added to a similar solution of corrosive sublimate, pearly crystals are immediately deposited, soluble in water and alcohol, and composed as above represented.

*Urea and Nitrate of Soda.*  $\text{NaO}, \text{NO}_5, + \text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2, + 2\text{HO}$ . This compound is deposited from a concentrated hot aqueous solution of its components, in the form of prismatic crystals, the solution of which may be boiled without decomposition.

*Urea and Nitrate of Lime.*  $\text{CaO}, \text{NO}_5, + 3[\text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2]$  This salt is formed by evaporating a mixture of the alcoholic solutions of nitrate of lime and urea, *in vacuo* over sulphuric acid; it forms glassy crystals, which explode when rapidly heated.

*Urea and Nitrate of Magnesia.*  $\text{MgO}, \text{NO}_5, + 2[\text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2]$  When an alcoholic solution of urea and nitrate of magnesia is slowly evaporated *in vacuo*, very deliquescent rhombic prisms having the preceding formula are deposited.

*Urea and Nitrate of Silver.*  $\text{AgO}, \text{NO}_5, + \text{C}_2 \text{H}_4 \text{O}_2 \text{N}_2$ . When concentrated aqueous solutions of equal atoms of urea and of nitrate of silver are mixed, either cold, or heated to  $120^\circ$ , prismatic crystals are immediately formed, soluble without decomposition in cold and hot water, and in alcohol; but when their dilute aqueous solution is long

boiled, it passes into carbonate of ammonia and cyanate of silver. There is also a crystallizable compound of 2 atoms of nitrate of silver with 1 of urea.

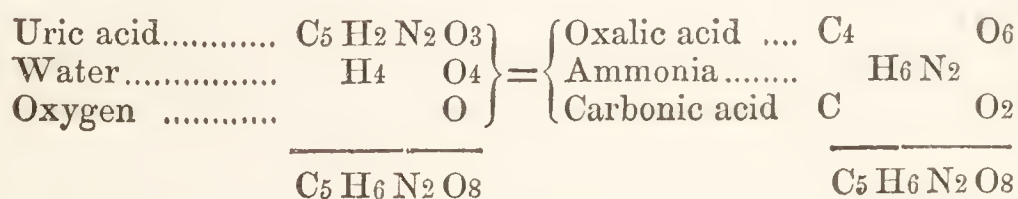
The combinations of *urea* with *nitrate of potassa*, *nitrate of baryta*, and *nitrate of strontia*, are also crystallizable.

URIC ACID. LITHIC ACID. URYLIC ACID.  $C_{10}H_4O_6N_4 = C_{10}H_2O_4N_4 + 2HO$ . This acid, which was discovered by Scheele in 1776, and which having been found in urinary *calculi*, was termed *lithic acid*, has been mentioned as an ingredient of human urine; it is also found in the urine of birds of prey, and of those which feed on fish and animal matter. The substance called *guano*\*, which is the decomposed excrement of aquatic birds, and which abounds in many of the small islands of the South Sea, and is used as a manure, also contains it; and it is found in the excrement of the parrot, and of some other birds which feed upon vegetables, and also in cantharides, and in the excrement of silk-worms. The excrement of large snakes, especially that of the *boa constrictor*, consists of white nodules containing little else than urate of ammonia. According to

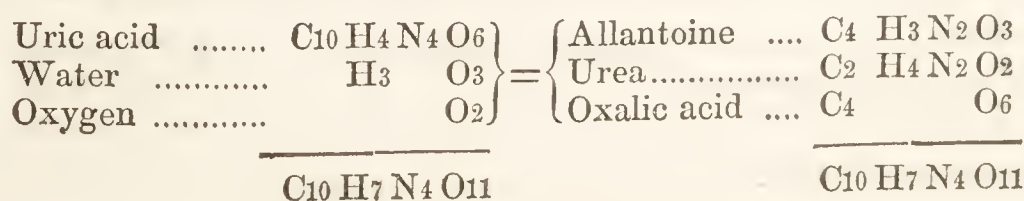
\* Of 2 specimens of *guano*, analyzed by Fownes, (*Mem. Chem. Soc.*, May, 1842,) No. 1 presented the aspect of a pale brown soft powder, with a few lumps, having in their inside whitish specks; its odor was exceedingly offensive; it yielded

|   |       |   |       |
|---|-------|---|-------|
| Oxalate of ammonia with traces of carbonate, undecomposed uric acid, brown organic matter and water ..... | 66.2  | No. 2. Darker in color, and having but little smell, contained no uric acid; it gave                      |       |
|   |       | Oxalate of ammonia with a little carbonate, organic matter, and water .....                               | 44.6  |
| Earthy phosphates with very little sandy matter .....   | 29.2  | Earthy phosphates, with a little gritty matter .....  | 41.2  |
|   |       | Alkaline sulphates, chlorides, and phosphates, (both of potassa and soda, the latter most abundant) ..... | 14.2  |
| Alkaline phosphate and chloride with little sulphate .....  | 4.6   |   |       |
|   | 100.0 |   | 100.0 |

The last specimen was evidently older and in a more advanced state of decomposition than the other; its odor less powerful and offensive; it contained no uric acid, but a larger proportion of inorganic substances. Fownes observes that there can be no doubt that the oxalate of ammonia is derived in some way or other from the uric acid contained in the excrement of the sea-birds, to the decomposition of which the guano deposits are due. We may imagine that in this mass of putrefying substance a decomposition of a peculiar kind may have been effected, perhaps somewhat after the following fashion:—



The only case in which oxalic acid is actually known to arise from uric acid, is in the artificial formation of allantoin, in which uric acid, water, and peroxide of lead being boiled together, give rise to oxalate of the protoxide of lead, allantoin, and urea; it is in short an oxidizing action, so far resembling the one imagined, but more complex



It is very unlikely that this peculiar mode of decomposition should occur under the



Mylius uric acid is also found in a glandular structure, immediately under the shell of certain land-snails (*Helix nemoralis, hortensis, &c.*) but not in water-snails. (*Erdmann and Marchand's Journ.*, xx. 509.) Uric acid has also been found in the fossil excrement (*coprolites*) of *Ichthyosauri*: specimens from Lyme Regis, analyzed by Girardin and Preisser (*Ann. Ch. et Ph.*, November, 1843) yielded phosphate of lime, carbonate of lime, urate of ammonia, urate of lime, silica, oxalate of lime, an alkaline sulphate, and scales.

*Uric acid* is best obtained from the above mentioned excrement of large snakes, which is voided in the form of a grey semifluid mass, and which is principally urate of ammonia; when dry it forms a whitish friable substance; this is reduced to powder and boiled, first in alcohol and then in water, to remove all matters soluble in those liquids; it may then be treated with dilute hydrochloric acid to remove phosphate of lime, washed, and digested in a hot solution of caustic potassa; the liquor is then poured off or filtered, more of the solution of potassa is added to it, and it is concentrated by evaporation, when the urate of potassa, which is not soluble in the strong alkaline liquor, separates, whilst the coloring matters are retained. On cooling, the whole concretes into a pasty mass, which must be pressed out and washed with cold water. The urate of potassa which remains is then dissolved in boiling water, and the hot solution poured into hydrochloric acid, when a white gelatinous precipitate falls, which soon assumes a crystalline aspect, and when washed and dried, is pure uric acid.

Bensch obtains uric acid by boiling the excrement of the snake in 30 or 40 parts of a weak solution of caustic potassa till the odor of ammonia is no longer perceived; the solution is then filtered, and a current of carbonic acid passed through it, till the precipitate, which is at first gelatinous, becomes crystalline, and the liquor is rendered nearly neutral to test paper. The precipitate, after having been well washed, is dissolved in very weak solution of potassa, and the uric acid thrown down by hydrochloric acid. (*Ann. der Pharm.*, liv. 189.)

Fritzsche dissolves uric calculi, or the snake's excrement, in warm concentrated sulphuric acid, and adds to the clear brownish and warm solution, small successive portions of water, as long as precipitation ensues: the precipitate is then washed, first with dilute sulphuric acid, and then with water, and dried.

Uric acid is a soft white crystalline powder; it is insipid and inodorous; it reddens moistened litmus-paper. It is almost insoluble in cold water, (requiring, according to Bensch, from 11,000 to 15,000 parts,)

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circumstances in which the guano is produced; urea certainly would not resist destruction a week, and no doubt the allantoine would share the same fate, and neither exist in the guano.

There is a curious relationship between the three bodies, oxalate of ammonia, oxamide, and allantoine, the only difference in composition being the diminishing proportion of the elements of water.

|  |   |
|--|---|
| Anhydrous oxalate of ammonia (doubled) ..... | C <sub>4</sub> H <sub>6</sub> N <sub>2</sub> O <sub>6</sub> |
| Oxamide (doubled).....                       | C <sub>4</sub> H <sub>4</sub> N <sub>2</sub> O <sub>4</sub> |
| Allantoine .....                             | C <sub>4</sub> H <sub>3</sub> N <sub>2</sub> O <sub>3</sub> |

(On the composition of South American guano, see DENHAM SMITH, *Mem. Ch. Soc.*, ii. 140.)

but soluble in between 1,800 and 1,900 parts of boiling water; it is insoluble in alcohol and in ether. When dried at  $212^{\circ}$ , this acid retains an atom of water, being  $= \text{C}_5 \text{H} \text{O}_2 \text{N}_2 + \text{HO}$ , if represented as a *monobasic* acid, or  $\text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4 + 2\text{HO}$ , if viewed as *bibasic*. The former view is adopted by Bensch; the latter by Liebig, according to which, the ultimate elements of the *hydrate of uric acid* are,

| Mitscherlich.              |    |     |     |     |        |     |        |       |                        |
|----------------------------|----|-----|-----|-----|--------|-----|--------|-------|------------------------|
| Carbon .....               | 10 | ... | 60  | ... | 35.71  | ... | 35.82  | } = { | Anhydrous<br>uric acid |
| Hydrogen ...               | 4  | ... | 4   | ... | 2.38   | ... | 2.38   |       |                        |
| Oxygen .....               | 6  | ... | 48  | ... | 28.58  | ... | 27.20  |       |                        |
| Nitrogen.....              | 4  | ... | 56  | ... | 33.33  | ... | 34.60  |       |                        |
| <hr/>                      |    |     |     |     |        |     |        |       |                        |
| Hydrated<br>uric acid....} | 1  |     | 168 |     | 100.00 |     | 100.00 | }     | Water.....             |
|                            |    |     |     |     |        |     |        |       |                        |
|                            |    |     |     |     |        |     |        | 1     | 168                    |
|                            |    |     |     |     |        |     |        |       | 100.00                 |

*Urates.* Liebig has the following observations on these salts. "Uric acid has a great tendency to form *acid* salts: Bensch has described the neutral and acid urates of potassa and soda; but the urates of ammonia, lime, baryta, strontia, and magnesia, are only as yet known as acid salts. Now since acid salts of these bases, except ammonia, only occur in the case of polybasic acids, we prefer to consider uric acid as *bibasic*." The general formula for the *neutral* urates is, according to Bensch,  $\text{MO} + \text{C}_5 \text{H} \text{O}_2 \text{N}_2$ ; or, on the bibasic hypothesis,  $2\text{MO}, + \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4$ . That for the *acid salts* is, according to Bensch,  $[\text{HO} + \text{C}_5 \text{H} \text{O}_2 \text{N}_2, + \text{MO} + \text{C}_5 \text{H} \text{O}_2 \text{N}_2]$ , or, on the other view,  $[\text{MO}, \text{HO}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4]$ . (*Turner's Chemistry*, p. 781.)

All the *urates* are very sparingly soluble in water, and are mostly, white insipid powders. By dry distillation they yield carbonate and hydrocyanate of ammonia, cyanic acid, and an empyreumatic oil; and those with alkaline bases leave cyanides. They are easily recognized by the action of nitric acid above described. These salts have been principally examined by Bensch, (*Ann. der Pharm.*, lviii.) and by Lipowitz, (*Ibid.*, xxxviii. 343).

*Urate of Ammonia.*  $\text{NH}_4 \text{O}, \text{HO}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4$ . When uric acid is digested in a solution of caustic ammonia, it becomes warm, and increases in bulk, forming, when dried, a white, amorphous, and very difficultly soluble salt. It may be obtained in very minute acicular crystals, by adding excess of ammonia to a boiling mixture of uric acid and water, and when dried at  $100^{\circ}$ , has the above composition. It requires 1608 parts of water at  $60^{\circ}$  for its solution. When long boiled in water it is decomposed, ammonia is evolved, and the pure acid remains.

*Urate of Potassa.*  $2\text{KO}, + \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4$ . When a solution of uric acid in a weak solution of potassa is evaporated, this salt separates in the form of a dense crystalline powder. It may be obtained in groups of acicular crystals, when cold dilute solution of potassa is saturated with uric acid, then heated to its boiling point, and mixed with twice its volume of boiling alcohol, and a strong solution of potassa dropped into it. This compound is alkaline; it dissolves in about 40 parts of boiling water, is very little soluble in alcohol, and insoluble in ether. Under the influence of carbonic acid, it passes into the acid salt. Heated to  $302^{\circ}$  it acquires a brown color, and at a higher temperature, blackens and fuses.



The *acid urate of Potassa*, (*binurate*),  $= \text{KO}, \text{HO}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4$ , separates in the form of a white granular powder, when carbonic acid is passed through a solution of uric acid in caustic potassa; and on boiling the liquor, the salt falls in the form of a flocculent precipitate, which dries into a mass. It is soluble in about 800 parts of cold, and from 70 to 80 parts of boiling water: it is insoluble in alcohol and in ether. It is tasteless, and its aqueous solution is neutral to tests, absorbs no carbonic acid, and is precipitated by sal ammoniac, by the salts of baryta, by carbonated alkalis, and by the salts of lead and of silver; but not by sulphate of magnesia.

*Urate of Soda*,  $2\text{Na O}, + \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4, + \text{HO}$ , is obtained as the potassa-salt: it forms a white powder, which, when heated to  $265^\circ$  loses 3.15 per cent.,  $= 1$  atom, of water. It is soluble in about 90 parts of boiling water; a little soluble in alcohol, and insoluble in ether: it may be heated to  $300^\circ$  without decomposition.

The *acid urate of Soda*,  $\text{Na O}, \text{HO}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4$ , is thrown down when carbonic acid is passed through a solution of the preceding salt. When bicarbonate of soda is added to a boiling solution of uric acid in caustic soda, this salt is obtained in delicate acicular crystals, which, at  $285^\circ$ , lose 1 atom of water. It is soluble in about 1200 parts of cold, and in 124 of boiling water: the solution is not alkaline, nor does it absorb carbonic acid.

The identity of *gouty concretions* of the joints, or of *chalk-stones*, as they are sometimes termed, with urate of soda, was shown by Wollaston in 1797: he observes that, when uric acid, soda, and a little warm water, are triturated together, a mass is formed, which, after the surplus of soda is washed off, possesses the chemical properties of those concretions. (*Phil. Trans.*, 1797, p. 386.)

*Urate of Lithia*.  $\text{LO}, \text{HO}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4$ . 1 part of carbonate of lithia, and 1 part of uric acid, readily dissolve in 90 parts of water at  $112^\circ$ . A boiling solution of 1 part of carbonate of lithia in 90 parts of water, dissolves 4 parts of uric acid, with the evolution of carbonic acid. On cooling, the solution becomes gelatinous, but again liquifies when heated. When excess of uric acid is digested in a hot solution of carbonate of lithia, urate of lithia is deposited, on cooling, in the form of a white granular crystalline salt. Dry urate of lithia dissolves in 60 parts of water at  $112^\circ$ , and again separates as the solution cools. The same salt is obtained by digesting uric acid in a solution of pure lithia. (LIPOWITZ.)

*Urate of Baryta*,  $\text{Ba O}, \text{HO}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4, + 2\text{HO}$ , is thrown down in the form of a white amorphous insoluble powder, on adding a hot solution of acid urate of potassa to chloride of barium. The corresponding *urates of lime*, and *strontia*, are similarly obtained.

*Urate of Magnesia*.  $\text{Mg O}, \text{HO}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4, + 6\text{HO}$ . When a hot solution of acid urate of potassa is added to sulphate of magnesia, groups of small crystals are after a time deposited, which are probably a double salt. When these are dissolved in boiling water, acicular crystals of the magnesian urate are deposited on cooling, which form a light powder when dried, soluble in about 4,000 parts of cold, and 170 of boiling water. This salt is neutral to tests, and insoluble in alcohol and ether. At  $338^\circ$  the crystals lose 19.2 per cent. of water,  $= 5$  atoms. At  $355^\circ$  decomposition begins.



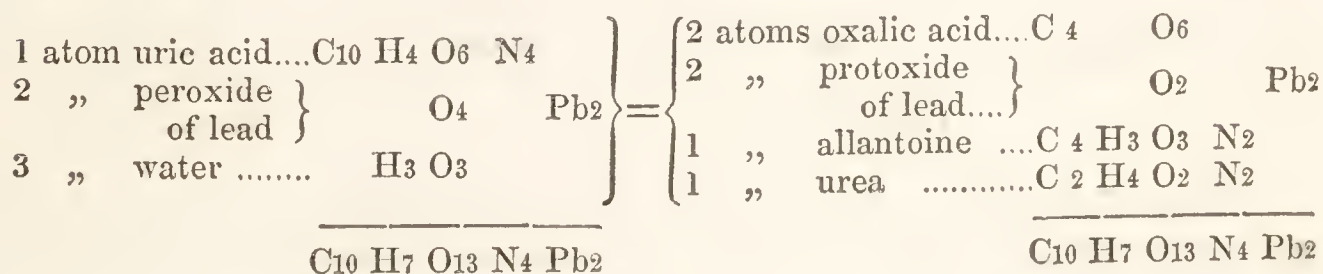
*Urate of Lead.*  $\text{Pb O}, \text{HO}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4, + \text{HO}$ . This salt falls in the form of a heavy white powder, when a saturated solution of the acid urate of potassa is added to acetate of lead.

*Urate of Copper.*  $3\text{Cu O}, \text{C}_{10} \text{H}_2 \text{O}_4 \text{N}_4, + 5\text{HO}$ . This salt is thrown down in the form of a green precipitate when solutions of sulphate of copper and acid urate of potassa are mixed. At a boiling heat it becomes brown, and dried over sulphuric acid it acquires a violet color. It loses 3 atoms of water when dried at  $284^\circ$ .

*Urate of Silver.* When a solution of acid urate of potassa is mixed with excess of nitrate of silver, a white gelatinous precipitate is formed, which soon blackens, especially if heated. If the uric solution be in excess, the precipitate remains white when dried. It is decomposed by a boiling heat.

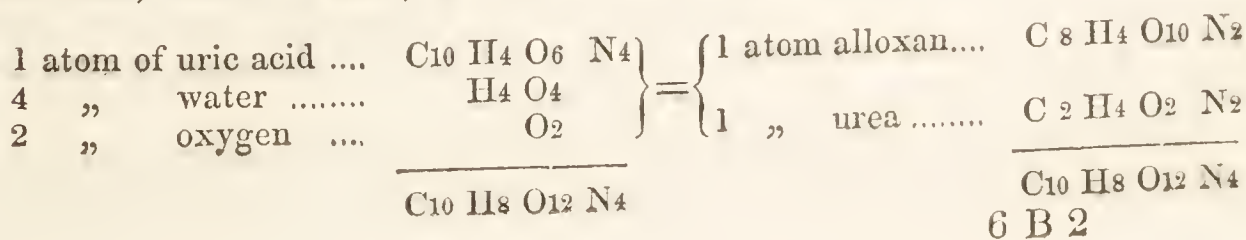
PRODUCTS OF THE DECOMPOSITION OF URIC ACID. When uric acid is heated in a retort, the products are carbonate of ammonia, hydrocyanic acid, and empyreumatic oil; a sublimate is afterwards formed composed of urea and cyanuric acid, and carbon remains. Heated in the open air uric acid evolves the odor of hydrocyanic and cyanic acids. (WÖHLER.)

When uric acid mixed with water is slowly heated up to the boiling-point, and peroxide of lead gradually added till its color is no longer destroyed, the products are allantoin, urea, oxalic acid, and some carbonic acid; the carbonic acid is evolved with effervescence, and the oxalic acid remains combined with the oxide of lead. According to Liebig, 1 atom of uric acid yields 1 atom of urea, 1 atom of allantoin, and 2 of oxalic acid.



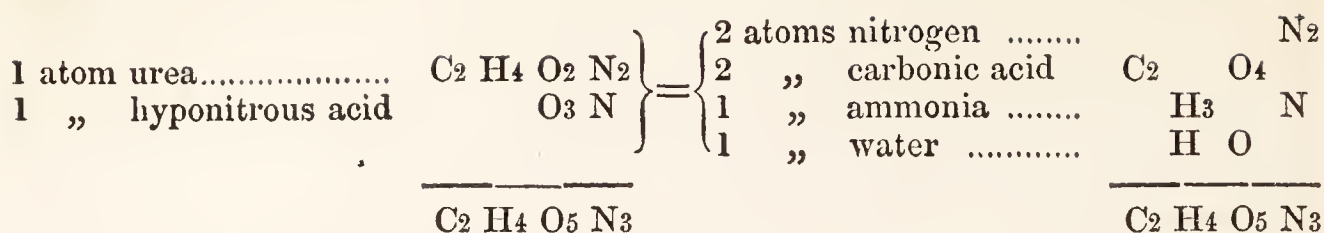
According to Pelouze, (*Ann. der Pharm.*, xlv. 108,) this decomposition of uric acid by peroxide of lead is not so definite as above represented, and is also attended by the production of *allanturic acid*  $= \text{C}_{10} \text{H}_7 \text{O}_9 \text{N}_4$ , a compound which also appears to have been obtained by Gregory, as a result of the oxidizement of uric acid by peroxide of manganese and permanganate of potassa.

When 1 part of uric acid is added by small portions at a time to 2 parts of nitric acid, sp. gr. 1.41 to 1.45, care being taken to prevent the heating of the mixture, nitrogen and carbonic acid (in equal volumes) are evolved, and at last the mixture becomes a crystalline magma, from the formation of *alloxan*. Nitrate of urea is probably first formed, which is decomposed by the evolved hyponitrous acid, and nitrate of ammonia, carbonic acid, and nitrogen are produced.

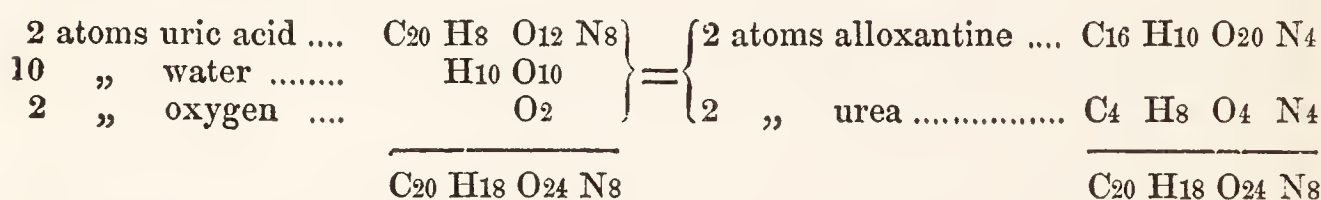




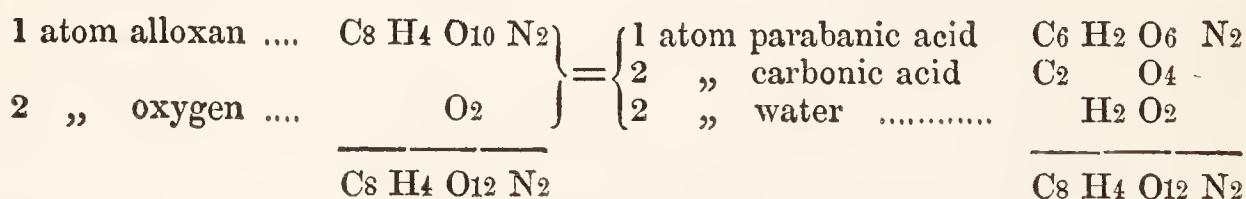
and



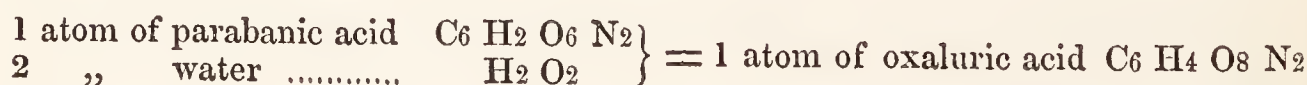
If the nitric acid, instead of being concentrated, be very dilute, the uric acid dissolves with effervescence, and *alloxantine*, nitrate of ammonia, and nitrate of urea, are found in solution. As in the former case, 1 atom of nitric acid loses 2 atoms of oxygen, which, acting upon 2 atoms of uric acid, form 2 of *alloxantine*, and 2 of urea; but as only 1 atom of hyponitrous acid is produced, only 1 atom of urea is converted into ammonia, carbonic acid, and nitrogen, and the other atom remains combined with the nitric acid.



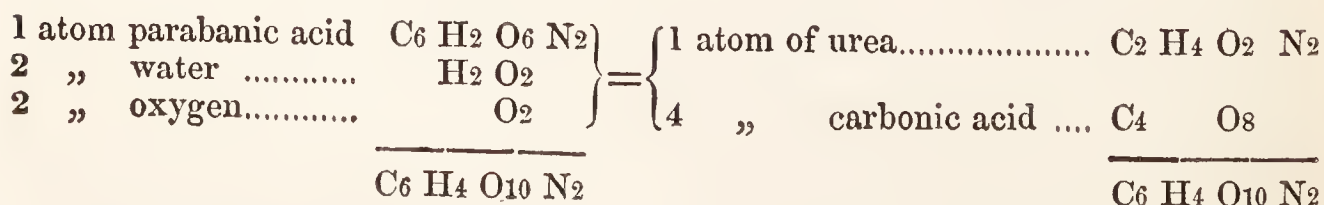
When a solution of uric acid in moderately strong nitric acid is evaporated down to a certain point, and till gas is no longer evolved, the alloxan originally produced is decomposed, and crystals of *parabanic acid* ( $\text{C}_6 \text{ H}_2 \text{ O}_6 \text{ N}_2$ ) are formed.



When the solution of parabanic acid is supersaturated with ammonia and evaporated, it combines with the elements of water to form *oxaluric acid*  $= \text{C}_6 \text{ H}_4 \text{ O}_8 \text{ N}_2$ .



When the nitric solution of parabanic acid, instead of being saturated with ammonia, is further evaporated, it continues to evolve carbonic acid, and ultimately yields crystals of *nitrate of urea*.



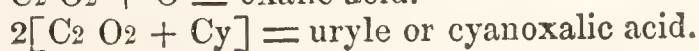
When the solution of uric acid in very dilute nitric acid, is evaporated till the alloxantine which it contains crystallizes, and then saturated with ammonia, the liquor acquires a purple color, and deposits *murexide*, together with a red powder, which is *uramile*.

When uric acid is dissolved in nitric acid, and the solution evaporated to dryness by a gentle heat, effervescence ensues, and a red compound

remains, which acquires a fine purple tint on the addition of ammonia. This is an effective test of the presence of minute quantities of uric acid. When uric acid is treated with chlorate of potassa and hydrochloric acid, it is resolved, according to Schlieper, (*Ann. der Pharm.*, lvi. 1,) into alloxan and urea.

When dry uric acid is heated in dry chlorine, cyanic acid and hydrochloric acid are the principal products, and there is a small quantity of carbonaceous residue. At common temperatures, dry chlorine has no action upon uric acid; but in the presence of moisture, it swells up, and carbonic and cyanic acids are evolved; on adding water, a solution of sal-ammoniac, with oxalic acid and hydrochloric acid, is obtained. (LIEBIG.)

The substances which I have now mentioned as results of the decomposition of uric acid, are themselves the sources of other compounds, so that the history of the derivatives of uric acid assumes a very complicated aspect. I shall follow Löwig in their enumeration, but shall consider uric acid and parabanic acid as *bibasic*, instead of adopting the monobasic equivalents, which he, upon the authority of Bensch, has assumed. (*Chem. der Organ. Verbind.*, ii. 1492.) It may be remarked that alloxan and alloxantine play an important part in these changes, and that those substances are easily transmutable into each other, their difference depending merely upon the presence of an additional atom of hydrogen in the latter. We are almost exclusively indebted to Liebig and Wöhler for the discovery of these curious products, and they derive them from an hypothetical radical, which they term *uryle*, or *cyanoxalic acid*, represented by the formula  $C_8 O_4 N_2$ , and which, they observe, may be considered as a compound of cyanogen and carbonic oxide,  $= 2Cy + 4CO$ ; or, as oxalic acid, in which, the oxygen united with the radical carbonic oxide, has been replaced by its equivalent of cyanogen.



Assuming the existence of *uryle*, and representing it by the symbol U1, the following compounds are represented by the annexed formulæ. (*Turner's Chem.*, edited by Liebig and Gregory, 8th ed., p. 779.)

| Rational formulæ.  | Names.                    | Empyrical formulæ.         |
|--|---------------------------|----------------------------|
| U1 + 1 atom of urea .....                                      | Uric acid .....           | $C_{10} H_4 O_6 N_4$       |
| U1 + O + 5HO .....   | Alloxantine .....         | $C_8 H_5 O_{10} N_2$       |
| U1 + O <sub>2</sub> + 4HO .....                                | Alloxan.....              | $C_8 H_4 O_{10} N_2$       |
| U1 + 4HO .....   | Dialuric acid.....        | $C_8 H_4 O_8 N_2$          |
| U1 <sub>3</sub> + 10HO .....                                   | 2 eq. Hydurylic acid..... | $2[C_{12} H_5 O_{11} N_3]$ |
| U1 + NO <sub>5</sub> + O <sub>3</sub> + 2HO .....              | Nitrohydurylic acid.....  | $C_8 H_2 O_{14} N_3$       |
| U1 + NH <sub>3</sub> + 2HO.....                                | Uramyle .....             | $C_8 H_5 O_6 N_3$          |
| U1 + O <sub>2</sub> + 4HO + NH <sub>3</sub> + 2SO <sub>2</sub> | Thionuric acid .....      | $C_8 H_7 O_{14} N_3 S_2$   |
| U1 + O <sub>2</sub> + 4HO + 2SO <sub>2</sub> .....             | Alloxanosulphurous acid   | $C_8 H_4 O_{14} N_2 S_2$   |

I have thought it right to insert the preceding tables of these compounds, in reference to the views of Liebig and Wöhler, and shall now proceed briefly to describe them, together with some other allied products not enumerated in the above list.

ALLANTOINE.  $C_4 H_3 O_3 N_2$ . This substance, formerly termed *allantoic acid*, was discovered by Vauquelin and Buniva, in the allantoic



fluid of the cow, (*Ann. de Chimie*, xxxiii. 279;) it is formed artificially as follows: 1 part of uric acid is boiled in 20 parts of water, and recently prepared and well washed peroxide of lead is added in successive portions to the hot liquor as long as its color is observed to change: it is then filtered, and evaporated till crystals form upon the surface, when it is set aside to cool: the deposited crystals are redissolved, and purified by recrystallization.

Allantoine forms small transparent rhombic prisms, inodorous, tasteless, and without action upon vegetable colors: they are very sparingly soluble in cold water, but dissolve in about 30 parts of boiling water. By dry distillation, allantoine yields carbonic and hydrocyanic acid, and ammonia, and leaves a porous coal. Heated with concentrated sulphuric acid allantoine yields carbonic oxide, carbonic acid, and sulphate of ammonia. Heated with caustic alkali it yields oxalic acid and ammonia. When nitrate of silver is dropped into a hot aqueous solution of allantoine, to which a little ammonia has been previously added, a white precipitate falls =  $C_8 H_5 O_5 N_4 + Ag O$ ; it therefore contains 2 equivalents of allantoine, 1 of oxide of silver, - 1 atom of water.

The ultimate elements of allantoine are equivalent to those of 2 atoms of cyanogen and 3 of water; it consists of

|                 |   |      |    |      |        | Wöhler and<br>Liebig. |
|-----------------|---|------|----|------|--------|-----------------------|
| Carbon .....    | 4 | .... | 24 | .... | 30·37  | .... 30·60            |
| Hydrogen .....  | 3 | .... | 3  | .... | 3·79   | .... 3·83             |
| Oxygen .....    | 3 | .... | 24 | .... | 30·37  | .... 30·12            |
| Nitrogen .....  | 2 | .... | 28 | .... | 35·47  | .... 35·45            |
| <hr/>           |   |      |    |      |        |                       |
| Allantoine..... | 1 |      | 79 |      | 100·00 | 100·00                |

ALLOXAN.  $C_8 H_4 O_{10} N_2$ . This term is applied by Wöhler and Liebig to the *erythric acid* of Brugnatelli. They obtained it, as above stated, by adding 1 part of uric acid in successive portions to 4 of nitric acid (specific gravity 1·45 to 1·5): it is dissolved with effervescence and evolution of heat, but the increase of temperature should be avoided by keeping the mixture cold, and adding the uric acid gradually. White and brilliant granular crystals are formed, and the liquid soon concretes; the crystalline mass should then be drained in a funnel, and afterwards dried on a porous brick, and purified by solution in water and recrystallization.

Schlieper obtains alloxan as follows: 4 ounces of uric acid are mixed in a basin with 8 ounces of hydrochloric acid, and 1 ounce of finely powdered chlorate of potassa is carefully added to the mixture: the mixture heats and thickens, but if the operation is properly conducted, neither chlorine nor carbonic acid are evolved; for this purpose, the chlorate should be very gradually added, under constant stirring. When from three-fourths to four-fifths of the chlorate are thus added, which should occupy half an hour, the hot fluid mixture should be diluted with twice its volume of cold water. In two or three hours, the undecomposed uric acid is deposited, and the solution of alloxan may be poured off and pressed out of it; the remaining uric acid is then treated as before, with hydrochloric acid and chlorate, great care being taken to avoid heating. Sulphuretted hydrogen is then passed through the solution of alloxan thus obtained, which converts it into alloxantine, which separates, whilst nitrate of urea remains in solution. A part of the alloxantine is now dissolved in



2 parts of water, heated to its boiling-point, and nitric acid dropped into it till nitric oxide escapes; more alloxantine is then added to the warm solution, as long as it is taken up; in this way the alloxantine is converted into alloxan, which crystallizes on cooling.

The following is Gregory's process for the preparation of alloxan (*Mem. Chem. Soc.*, iii. 43):—

“2 or  $2\frac{1}{2}$  fluid ounces of colorless nitric acid, sp. gr. 1.412, are placed in a flat-bottomed dish or beaker glass, and as much uric acid is introduced as will lie on the point of a small spatula. This is well stirred in to prevent the formation of lumps, and in a few minutes effervescence commences, the liquor becomes slightly warm, and the powder dissolves. More uric acid is now added, taking care never to exceed a certain small quantity, and not to allow the liquid to become warm beyond a certain degree, which is easily judged of by laying the dish on the hand. If too hot when uric acid is added, or if too much acid be added at once, the uniform steady effervescence is changed into a violent and tumultuous action, after which no alloxan can be obtained. It is proper to have a plate with cold water at hand, in which to place the dish or glass if it should seem likely to become too warm. But a little practice enables us to regulate the operation so that no external cooling is required.

“After several portions of uric acid have been added, crystals of alloxan begin to appear in the warm liquid, but the addition of uric acid is to be continued, with the same precautions, till so much alloxan has been formed, that on cooling the whole becomes nearly semisolid. When this point is reached, the liquid has become somewhat viscid, and this, along with the presence of the crystalline deposit of alloxan, gives a peculiar character to the effervescence toward the end of the operation. I commonly find that with  $2\frac{1}{2}$  fluid ounces of nitric acid, the point above alluded to is reached when about 1,200 grains of uric acid dried at  $212^{\circ}$  have been dissolved. It does not answer to operate on a much larger scale; it is better to use several dishes at once, each containing  $2\frac{1}{2}$  or at the most 3 fluid ounces of acid. For every 500 grains of uric acid 1 fluid ounce of nitric acid may be allowed.

“The whole is now allowed to stand all night in a cool place, and next day the alloxan is collected on a funnel with the aid of a little asbestos. The mother-liquid drains off, and the last portions of it are cautiously displaced by ice-cold water, till the droppings are found to have only a moderately strong acid taste. The alloxan on the funnel, which is anhydrous, is then digested with just as much water at  $140^{\circ}$  or  $150^{\circ}$  F. as will dissolve it. The solution is filtered, and on cooling deposits a large crop of crystals of hydrated alloxan. [Should too much water have been added, the filtered liquid must be evaporated at from  $120^{\circ}$  to  $140^{\circ}$  F., till on cooling, it crystallizes abundantly.] The mother-liquid of these crystals, evaporated at the same temperature, yields a second crop. The mother-liquor of this is added to the acid mother-liquor previously drained off, and the whole liquid treated, after the addition of two or three times its bulk of water, with sulphuretted hydrogen, till the alloxan present is reduced to the state of alloxantine. As a part is always reduced still further, to dialuric acid, the liquid must be exposed to the air for a day or two, or until it deposits no more crystals. The alloxantine is purified



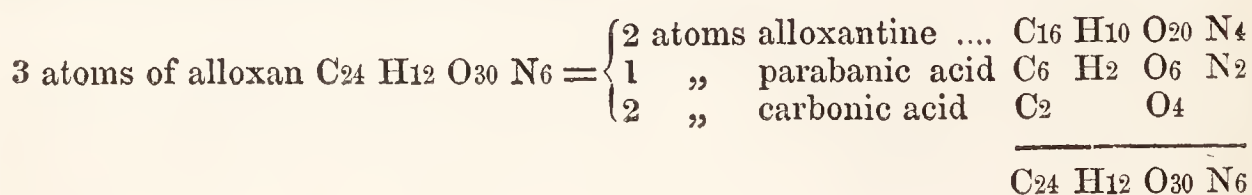
by solution in boiling water, filtration to separate sulphur, and crystallization; and when dry, three parts of it correspond to rather more than four of hydrated alloxan. The mother-liquid of the alloxantine generally yields some parabanic acid; but very little if the process has been carefully performed."

*Alloxan* crystallizes at common temperatures, with 6 atoms of water of crystallization; the crystals are large, and derived from a rhombic octohedron. The crystals deposited from a hot solution, are anhydrous, and derived from an oblique prism. Alloxan is readily soluble in water, and the solution tinges the cuticle purple, and communicates to it a peculiar odor; it has an unpleasant acid-saline and metallic taste, and reddens litmus, but does not form salts with bases.

Alloxan consists of

|                         |    |      |     |      |       | Wöhler and<br>Liebig. |
|-------------------------|----|------|-----|------|-------|-----------------------|
| Carbon .....            | 8  | .... | 48  | .... | 30.0  | .... 30.38            |
| Hydrogen .....          | 4  | .... | 4   | .... | 2.5   | .... 2.57             |
| Oxygen .....            | 10 | .... | 80  | .... | 50.0  | .... 49.09            |
| Nitrogen .....          | 2  | .... | 28  | .... | 17.5  | .... 17.96            |
| <hr/>                   |    |      |     |      |       |                       |
| Anhydrous alloxan ..... | 1  |      | 160 |      | 100.0 | 100.00                |

By long boiling, an aqueous solution of alloxan yields alloxantine, parabanic acid, and carbonic acid.



When alloxan, in aqueous solution, is oxidized by peroxide of lead, it yields urea and carbonic acid:  $C_8 H_4 O_{10} N_2 + O_4 = C_2 H_4 O_2 N_2 + 6CO_2$ . When heated with strong nitric acid, it is converted into parabanic acid and carbonic acid. The electrolysis of an aqueous solution of alloxan yields oxygen at the positive electrode, and crystals of alloxantine are formed at the negative electrode.

When sulphuretted hydrogen is passed through a cold solution of alloxan, sulphur is precipitated, and alloxantine formed; but if the solution be boiling hot, the alloxantine passes into another substance, which remains in solution, but which, on the addition of alloxan, yields alloxantine; hence it is probable that the substance last formed, contains more hydrogen than alloxantine.

**ALLOXANIC ACID.**  $C_8 H_4 O_{10} N_2$ ;  $= C_8 H_2 O_8 N_2 + 2HO$ . This acid is regarded by Wöhler and Liebig as *bibasic*; it is produced by the action of alkalis upon alloxan, and is best obtained by gradually adding baryta water to a warm solution of alloxan, till it begins to become turbid; on cooling, crystals of *alloxanate of baryta* separate, which are to be decomposed by dilute sulphuric acid; the filtrate, on careful evaporation to the consistence of syrup, yields a crystalline mass of hydrated alloxanic acid.

This acid crystallises in groups of small prisms; it has a sour, and at the same time slightly sweet taste; it is very soluble in water, and soluble in

5 or 6 parts of alcohol. When heated it fuses, and evolves cyanic acid vapor. The aqueous solution of alloxanic acid, when heated to its boiling-point, gives off carbonic acid, and *leucoturic acid* =  $C_6H_3O_6N_2$ , and *difluan* =  $C_6H_4O_5N_2$ , are at the same time formed. Heated with nitric acid, alloxanic acid passes into parabanic acid. It will be seen by the above formula, that the ultimate elements of the *hydrated alloxanic acid* are also those of *anhydrous alloxan*. Hence we have—

|                                  |    |     |     |     |       |       |                                     |   |     |     |     |        |
|----------------------------------|----|-----|-----|-----|-------|-------|-------------------------------------|---|-----|-----|-----|--------|
| Carbon.....                      | 8  | ... | 48  | ... | 30.0  | } = { | Anhydrous allox-<br>anic acid ..... | 1 | ... | 142 | ... | 88.75  |
| Hydrogen .....                   | 4  | ... | 4   | ... | 2.5   |       |                                     |   |     |     |     |        |
| Oxygen .....                     | 10 | ... | 80  | ... | 50.0  |       |                                     |   |     |     |     |        |
| Nitrogen .....                   | 2  | ... | 28  | ... | 17.5  |       |                                     |   |     |     |     |        |
| <hr/>                            |    |     |     |     |       |       |                                     |   |     |     |     |        |
| Hydrated alloxanic<br>acid ..... | 1  |     | 160 |     | 100.0 |       |                                     | 1 |     | 160 |     | 100.00 |

*Alloxanates.* Alloxanic acid decomposes the carbonates and acetates; it dissolves zinc and cadmium with the evolution of hydrogen gas. It forms neutral, basic, and acid salts. When neutralized by ammonia it forms a white precipitate with the salts of silver, which becomes yellow and then black, and effervesces, when boiled. With ammonia in excess it forms white precipitates with the salts of lime, baryta, and strontia, which are soluble in excess of acid. The solutions of the neutral alloxanates of lime, baryta, and strontia, become turbid when boiled, and urea and mesoxalic acid are formed. These salts have been examined by Schlieper.

*Alloxanate of Ammonia.*  $NH_4O, HO, C_8H_2O_8N_2$ . This, which is the acid salt, (binalloxanate), forms transparent prismatic crystals, soluble in 3 parts of water, but insoluble in alcohol. It is resolved, by dry distillation, into ammonia, carbonic acid, cyanic acid, hydrocyanic acid, oxamide, and urea. When its concentrated aqueous solution is saturated with ammonia, and mixed with alcohol, the *neutral alloxanate*, =  $2NH_4O, C_8H_2O_8N_2$ , is thrown down: on evaporating its solution, ammonia escapes, and the acid salt is reproduced.

*Alloxanate of Potassa.* (*neutral.*)  $2KO, C_8H_2O_8N_2, + 6HO$ . A concentrated solution of alloxan is mixed with an equal volume of a strong solution of caustic potassa, and alcohol is added till a permanent precipitate ensues, when, after some hours, crystals of the above salt are formed; they are readily soluble in water, but insoluble in alcohol and ether; when heated to  $212^\circ$  they lose 5 equivalents of water, and at  $300^\circ$  become anhydrous.

The *acid alloxanate of Potassa*,  $KO, HO, C_8H_2O_8N_2$ , is similarly prepared, only with excess of alloxan, using 4 volumes of its solution to 1 volume of the solution of potassa: on adding excess of alcohol, it falls as a crystalline powder, sparingly soluble in water. When its aqueous solution is evaporated, a gum-like mass is obtained, which, after long standing, reverts to the crystalline modification.

*Alloxanate of Soda* is a very soluble deliquescent salt, very difficultly crystallizable.

*Alloxanate of Lime.*  $2CaO, C_8H_2O_8N_2, + 5HO$ . When a concentrated solution of alloxanate of potassa is added to chloride of calcium, a granular precipitate falls, very soluble in water, but insoluble in alcohol. At  $212^\circ$  it parts with its water of crystallization. The *acid salt*,



$\text{CaO}$ ,  $\text{HO}$ ,  $\text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2$ ,  $+ 5\text{HO}$ , forms transparent crystals, which rapidly effloresce; they are soluble in 20 parts of water, and also in alcohol.

*Alloxanate of Baryta*,  $2\text{BaO}$ ,  $\text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2$ ,  $+ 4\text{HO}$ , is obtained by adding baryta-water to a solution of alloxan, heated to  $140^\circ$ , till a permanent precipitation ensues, when the liquor is allowed to cool: the salt forms short needles, or pearly scales, which lose 3 atoms of water at  $212^\circ$ , and at  $300^\circ$  become anhydrous: they are sparingly soluble in cold water. Heated to redness, they leave carbonate of baryta and cyanide of barium. The *acid alloxanate*,  $\text{BaO}$ ,  $\text{HO}$ ,  $\text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2$ ,  $+ 2\text{HO}$ , is best formed by adding chloride of barium to a solution of acid alloxanate of ammonia; it forms a crystalline powder, soluble in water and in alcohol.

The remaining alloxanates described by Schlieper are constituted as follows:—

|   |  |
|---|--|
| <i>Alloxanate of magnesia</i> .....         | $2\text{Mg O}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + 5\text{HO}$           |
| <i>Alloxanate of nickel</i> .....           | $2\text{Ni O}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + 2\text{HO}$           |
| <i>Alloxanate of zinc</i> (basic) .....     | $3\text{Zn O}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + 8\text{HO}$           |
| "    "    (acid) .....                      | $\text{Zn O}, \text{HO}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + 4\text{HO}$ |
| <i>Alloxanate of lead</i> (neutral) .....   | $2\text{Pb O}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + 2\text{HO}$           |
| "    "    (basic) .....                     | $3\text{Pb O}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + 2\text{HO}$           |
| "    "    (acid) .....                      | $\text{Pb O}, \text{HO}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + 2\text{HO}$ |
| <i>Alloxanate of copper</i> (basic) .....   | $3\text{Cu O}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + \text{HO}$            |
| "    "    (neutral) .....                   | $2\text{Cu O}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2 + 8\text{HO}$           |
| <i>Alloxanate of silver</i> (neutral) ..... | $2\text{Ag O}, \text{C}_8 \text{H}_2 \text{O}_8 \text{N}_2$                        |

ALLOXANTINE.  $\text{C}_8 \text{H}_5 \text{O}_{10} \text{N}_2$ . This compound was first described by Prout, among the products of the decomposition of uric acid by nitric acid; it is formed by the action of deoxidizing agents, such as nascent hydrogen, sulphuretted hydrogen, or chloride of tin, upon hydrated alloxan, its relation to alloxan resembling that of indigo-white to indigo-blue.

Alloxantine is obtained, 1, *from uric acid*: 1 part of this acid is added to 32 parts of boiling water, and dilute nitric acid is then added in successive portions till a solution is obtained, which, when evaporated to about two-thirds of its volume, gradually deposits crystals of alloxantine: they require to be purified by recrystallization. 2. *from alloxan*: a solution of alloxan, or the acid mother-liquor of alloxan above mentioned, is subjected to a current of sulphuretted hydrogen gas; sulphur is first deposited, and then white crystals of alloxantine. When a large quantity has formed, it is collected, with the sulphur, on a filter, washed with a little cold water, and the filter with its contents then boiled with a large quantity of water. The solution, filtered while hot, and with the addition of a few drops of hydrochloric acid, deposits on cooling, a large crop of crystals of pure alloxantine. The acid liquid filtered from the first deposit, often, on standing a day or two, deposits a large additional quantity of alloxantine: this always happens if too much sulphuretted hydrogen has been used; for that converts alloxantine partially into dialuric acid, which is more soluble, and which, by absorbing oxygen from the air, is reconverted into alloxantine, and so deposited. (GREGORY.)

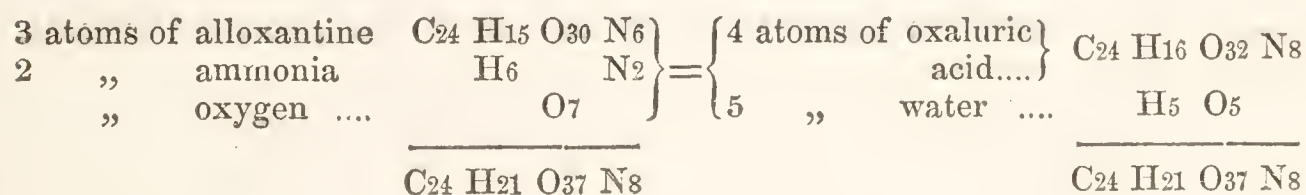
In the conversion of alloxan into alloxantine, by sulphuretted hydrogen, the alloxan acquires an atom of hydrogen; and oxidizing agents reconvert alloxantine into alloxan, by converting this hydrogen into water.  $\text{C}_8 \text{H}_5 \text{O}_{10} \text{N}_2 + \text{O} = \text{C}_8 \text{H}_4 \text{O}_{10} \text{N}_2 + \text{HO}$ .



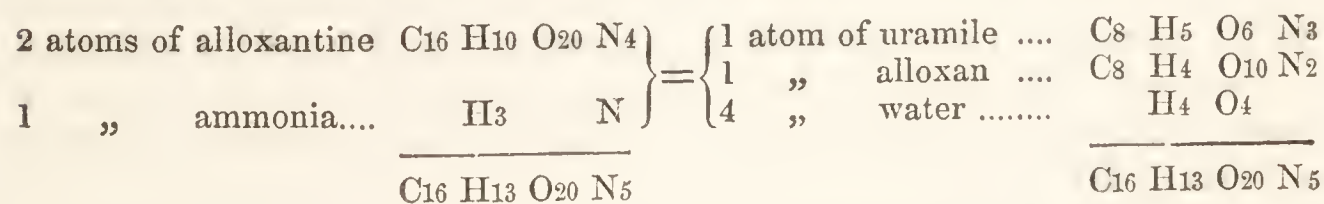
*Alloxantine* forms small brilliant prismatic crystals, sparingly soluble in cold water, but more soluble in hot water. Heated to  $212^{\circ}$  they lose no weight, but at  $300^{\circ}$  they lose 3 atoms of water. They are colorless, or slightly yellow, but in an ammoniacal atmosphere they acquire a red tint, and afterwards a greenish and somewhat metallic lustre. Alloxantine reddens litmus, but has no other characters of an acid. It is especially characterized by giving a violet-colored precipitate with baryta water, which, by excess of baryta, becomes white, and when heated, dissolves. It throws down a black powder of silver from nitrate of silver, and passes into alloxan, or oxaluric acid. Anhydrous alloxantine consists of

|                            |    |     |     |     |        | Wöhler and<br>Liebig. |
|----------------------------|----|-----|-----|-----|--------|-----------------------|
| Carbon .....               | 3  | ... | 48  | ... | 29.81  | 30.339                |
| Hydrogen .....             | 5  | ... | 5   | ... | 3.10   | 3.200                 |
| Oxygen .....               | 10 | ... | 80  | ... | 49.67  | 48.792                |
| Nitrogen .....             | 2  | ... | 28  | ... | 17.42  | 17.669                |
| <hr/>                      |    |     |     |     |        | <hr/>                 |
| Anhydrous alloxantine..... | 1  |     | 161 |     | 100.00 | 100.000               |

When an ammoniacal solution of alloxantine is evaporated in the contact of air, oxygen is absorbed, and if the residue be redissolved in ammonia, and again evaporated, it is ultimately changed into crystals of *oxalurate of ammonia*.



When an aqueous solution of alloxantine is boiled out of contact of air, it becomes purple, but this color soon disappears, uramile is deposited, and the yellow mother-liquor yields crystals of murexide. When hot solutions of alloxantine and sal ammoniac, in water free from air, are mixed, the liquor becomes purple, and then colorless; uramile falls down, and alloxan and hydrochloric acid remain in solution.



When nitric acid, and then ammonia, are dropped into a warm solution of alloxantine, a solution of a more permanent purple color, containing murexide, is obtained.

When a solution of alloxantine, mixed with excess of hydrochloric acid, is rapidly evaporated to a small bulk, and the residue, when cold, treated with nitric acid, a new acid, *allituric acid*  $= \text{C}_6 \text{ H}_2 \text{ O}_3 \text{ N}_2$ , + HO, is formed. In the nitric solution we find alloxan, parabanic acid, and *dilituric acid*,  $= \text{C}_8 \text{ H}_2 \text{ O}_9 \text{ N}_3$ . This last acid is also obtained when a solution of alloxan is treated with sulphuretted hydrogen, so as to form alloxantine; the filtered mother-liquor then yields diliturate of ammonia, and afterwards parabanic acid, on evaporation.

It has been above stated that baryta-water produces a blue precipitate



in a recent solution of alloxantine, which soon becomes colorless; after some time, alloxanate of baryta separates. If the solution of alloxantine be left some time to itself, and then tested by baryta-water, there is no violet precipitate, and on evaporation, crystals having the properties of alloxanic acid are obtained. Acetate of lead added to an aqueous solution of alloxantine, produces a white precipitate, containing 66 *per cent.* of oxide of lead; and if the supernatant liquor be boiled, a granular salt containing 88 *per cent.* of oxide of lead, falls. (FRITZSCHE.)

**THIONURIC ACID.**  $C_8 H_5 O_{12} N_3 S_2 + 2HO = C_8 H_5 O_6 N_3 + 2SO_3 + 2HO$ . To obtain this acid, a saturated aqueous solution of sulphurous acid is added to a cold solution of alloxan, in such proportion as to leave a distinct odor of sulphurous acid; excess of carbonate of ammonia, mixed with a little caustic ammonia, is then added, and the whole boiled for a few minutes. On cooling, colorless crystals of *thionurate of ammonia* are deposited, which by recrystallization acquire a pink tint. A solution of this salt added to acetate of lead, throws down *thionurate of lead*, which at first is gelatinous, but soon becomes dense and crystalline. The solution of this salt is decomposed by sulphuretted hydrogen, filtered and evaporated; it leaves the *hydrated thionuric acid*, in the form of a white crystalline mass, very soluble in water, and of a strong acid taste. When its aqueous solution is boiled, it is resolved into *uramile* and sulphuric acid. The elements of thionuric acid, as it exists in combination, may be represented as

|                                |   |     |     |     |        |
|--------------------------------|---|-----|-----|-----|--------|
| Carbon .....                   | 8 | ... | 48  | ... | 21.52  |
| Hydrogen .....                 | 5 | ... | 5   | ... | 2.24   |
| Oxygen .....                   | 6 | ... | 48  | ... | 21.52  |
| Nitrogen .....                 | 3 | ... | 42  | ... | 18.74  |
| Sulphuric acid .....           | 2 | ... | 80  | ... | 35.98  |
| <hr/>                          |   |     |     |     |        |
| Anhydrous thionuric acid ..... | 1 |     | 223 |     | 100.00 |

*Thionurate of Ammonia*,  $2NH_4 O + \overline{Thi}$ , obtained as above described, crystallizes in nacreous scales containing 2 atoms of water of crystallization, which they lose when dried at  $212^\circ$ , and acquire a pink tint. If to a solution of this salt, a quantity of hydrochloric acid be added sufficient to neutralize half the ammonia which it contains, and evaporated upon a water-bath, acicular crystals of the *acid thionurate of ammonia* are formed,  $= NH_4 O, HO, + \overline{Thi}$ .

*Thionurate of Lime*, prepared by mixing hot solutions of nitrate of lime and thionurate of ammonia, crystallizes in silky acicular prisms.

*Thionurate of Baryta*, formed by double decomposition, appears at first as a gelatinous mass, which afterwards becomes transparent and crystalline. It is easily soluble in nitric and hydrochloric acid.

*Thionurate of Lead* has been above adverted to; its crystals become pink when dried, and when subjected to destructive distillation they yield urea, and a peculiar crystallizable product.

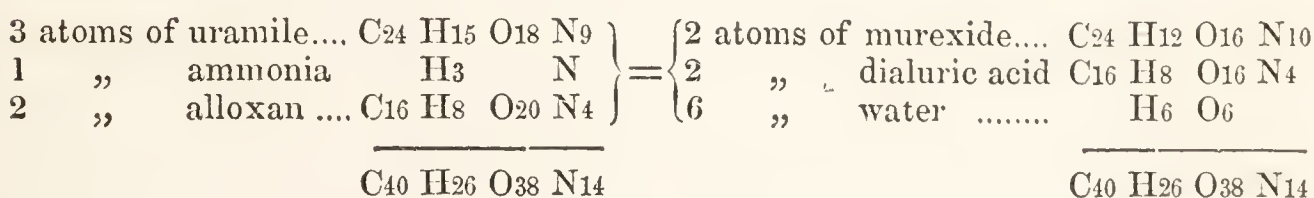
*Thionurate of Zinc* forms small crystalline groups of a pale yellow color.

**URAMILE.**  $C_8 H_5 O_6 N_3$ . When a solution of thionurate of ammonia, acidulated by hydrochloric acid, is boiled till it begins to become turbid,

the whole soon thickens, in consequence of the separation of crystalline uramile, which is insoluble in hot water, but readily soluble in ammonia and the fixed alkalis, and the acids again precipitate it in silky acicular crystals, composed of

|                |   |      |     |      |        | Liebig and<br>Wöhler. |
|----------------|---|------|-----|------|--------|-----------------------|
| Carbon.....    | 8 | .... | 48  | .... | 33.56  | .... 33.513           |
| Hydrogen ..... | 5 | .... | 5   | .... | 3.49   | .... 3.785            |
| Oxygen .....   | 6 | .... | 48  | ..   | 33.56  | .... 33.521           |
| Nitrogen ..... | 3 | .... | 42  | .... | 29.39  | .... 29.181           |
| <hr/>          |   |      |     |      |        | <hr/>                 |
| Uramile .....  | 1 |      | 143 |      | 100.00 | 100.000               |

An ammoniacal solution of uramile reddens on exposure to air, and when evaporated in contact of air it absorbs oxygen, and forms *murexide*,  $C_{12}H_6O_8N_5$ . When a solution of alloxan is added to an ammoniacal solution of uramile the results are *murexide* and dialuric acid.



Uramile is soluble, without decomposition, in concentrated sulphuric acid. Concentrated nitric acid converts it into alloxan.

A saturated solution of uramile in hot dilute caustic potassa, absorbs oxygen, and in the course of 12 or 14 hours deposits murexide.

**URAMILIC ACID.**  $C_{16}H_{10}O_{15}N_5$ . When a cold saturated solution of thionurate of ammonia is acidulated by sulphuric acid, and then slowly evaporated, it yields *uramilic acid*: it crystallizes in slender colorless prisms, which redden when dried. It is soluble in about 8 parts of cold water, but much more soluble in hot water; it has a feeble acid taste and reaction. When long boiled with dilute sulphuric acid, it yields dimorphous alloxantine. It is decomposed, and converted into a peculiar crystallizable compound, when treated with nitric acid. The *uramilates* of the alkalis are easily soluble; those of the earths less so, and that of oxide of silver is insoluble in water. Uramilic acid consists of

|                     |    |      |     |      |        | Wöhler and<br>Liebig. |
|---------------------|----|------|-----|------|--------|-----------------------|
| Carbon .....        | 16 | .... | 96  | .... | 32.43  | .... 32.40            |
| Hydrogen .....      | 10 | .... | 10  | .... | 3.37   | .... 3.62             |
| Oxygen .....        | 15 | .... | 120 | .... | 40.54  | .... 40.75            |
| Nitrogen .....      | 5  | .... | 70  | .... | 23.66  | .... 23.23            |
| <hr/>               |    |      |     |      |        | <hr/>                 |
| Uramilic acid ..... | 1  |      | 296 |      | 100.00 | 100.00                |

**OXALURIC ACID.**  $C_6H_3O_7N_2 + HO$ . This acid is formed as above stated, when an ammoniacal solution of alloxantine is evaporated under exposure to air. The oxalurate of ammonia so obtained, is dissolved in hot water, and sulphuric or hydrochloric acid added; this mixture is then cooled as rapidly as possible, when the oxaluric acid is deposited in the form of a white crystalline powder: it should be washed with cold water till the washings, when neutralized by ammonia, cause a precipitate with



the salts of lime which is readily redissolved by heat. Oxaluric acid is also formed when a solution of parabanic acid, supersaturated by ammonia, is evaporated by heat: on cooling, the crystals which are deposited are those of oxalurate of ammonia.

Oxaluric acid is a white or slightly yellow crystalline powder; it reddens vegetable blues, but has no acid taste, and is difficultly soluble in cold water. When neutralized by ammonia, it forms a white precipitate in a solution of nitrate of silver, which redissolves on heating the liquor. When long boiled with water, it is resolved into oxalic acid and oxalate of urea.  $C_6 H_3 O_7 N_2 = 2[C_2 O_3] + C_2 H_4 O_2 N_2$ .

This acid consists, when *anhydrous*, of

|                              |   |      |     |      |        | Wöhler and<br>Liebig. |
|------------------------------|---|------|-----|------|--------|-----------------------|
| Carbon.....                  | 6 | .... | 36  | .... | 29.28  | .... 29.225           |
| Hydrogen .....               | 3 | .... | 3   | .... | 2.44   | .... 2.427            |
| Oxygen .....                 | 7 | .... | 56  | —    | 45.52  | .... 45.389           |
| Nitrogen .....               | 2 | .... | 28  | .... | 22.76  | .... 22.959           |
| <hr/>                        |   |      |     |      |        |                       |
| Anhydrous oxaluric acid .... | 1 |      | 123 |      | 100.00 | 100.000               |

*Oxalurates.* The oxalurates of the alkalis are very soluble, but those of the alkaline earths very sparingly soluble. When strong solutions of oxalurate of ammonia and chloride of calcium, or chloride of barium, are mixed, small brilliant crystals of the earthy salts are deposited. When excess of ammonia is added to a solution of oxalurate of lime, a basic salt falls, in the form of a gelatinous precipitate, which is redissolved by excess of water.

*Oxalurate of Ammonia.*  $NH_4 O + C_6 H_3 O_7 N_2$ . This salt is best prepared, according to Liebig, by treating a recently-made solution of uric acid in dilute nitric acid, with an excess of ammonia, and evaporating: the liquid at first becomes purple, but afterwards colorless, and when duly concentrated and then cooled, deposits radiated groups of hard acicular yellow crystals, which may be rendered colorless by charcoal and recrystallization. This salt is also formed, when a solution of parabanic acid is heated with ammonia.

Oxalurate of ammonia forms groups of silky crystals, difficultly soluble in cold, but readily in hot water. The solution is neutral to tests, and may be boiled and evaporated without decomposition. The dry salt loses no weight till heated to above  $250^{\circ}$ , when it is rapidly decomposed, forming hydrocyanic acid, ammonia, and oxamide. (GREGORY.)

*Oxalurate of Silver*,  $Ag O + C_6 H_3 O_7 N_2$ , is obtained by mixing boiling solutions of nitrate of silver and oxalurate of ammonia; it is deposited as the liquor cools, in long anhydrous needles, of a silky lustre, which are decomposed without explosion, by heat.

**DIALURIC ACID.**  $C_8 H_3 O_7 N_2 + HO$ . This acid is formed when sulphuretted hydrogen is passed through a boiling solution of alloxan, or alloxantine, till the liquor acquires a decided acid reaction, and sulphur is no longer precipitated; it is then neutralized by carbonate of ammonia, filtered, and evaporated, when it leaves *dialurate of ammonia*. The same salt is also formed when sulphuret of ammonia is added to a solution of alloxan or alloxantine; a crystalline precipitate then falls, which, when boiled in the liquor, redissolves, and is again deposited on cooling in minute silky



prisms, which become red on drying: they should be washed upon the filter, first with dilute sulphuret of ammonia, and then with alcohol to which a little of the sulphuret has been added, and dried by pressure in blotting paper, and then *in vacuo*: they may thus be obtained nearly white, and when once dry, they are permanent. When this salt is dissolved in hot and moderately strong hydrochloric acid, crystals of *dialuric acid* are deposited on cooling. They somewhat resemble those of alloxantine, but are larger and less brilliant. Their solution, and the crystals themselves under water, absorb oxygen, and are soon changed into alloxantine, from which dialuric acid only differs by 1 atom of oxygen and 1 of water. This is a powerful acid: its salts are insoluble, or sparingly soluble in water, and only permanent in the dry state. (GREGORY.)

MYKOMELINIC ACID,  $C_8 H_5 O_5 N_4$ , is a product of the mutual action of ammonia and alloxan. It is prepared by heating a solution of alloxan with excess of ammonia to its boiling-point, then adding excess of dilute sulphuric acid, and boiling for a short time, when the *mykomelinic acid* forms a gelatinous precipitate, which dries into a yellow powder. It is sparingly soluble in cold water, and has an acid reaction: it is soluble in ammonia, and in the fixed alkalis, but does not form crystallizable salts. *Mykomelinate of silver* is a yellow insoluble powder.

This acid is produced by the action of 2 atoms of ammonia upon 1 of alloxan.  $2 [NH_3] + C_8 H_4 O_{10} N_2 = C_8 H_5 O_5 N_4 + 5HO$ . It consists of

|                       |   |     |     |     |        | Wöhler and<br>Liebig. |         |
|-----------------------|---|-----|-----|-----|--------|-----------------------|---------|
| Carbon.....           | 8 | ... | 48  | ... | 32·21  | ...                   | 32·877  |
| Hydrogen .....        | 5 | ... | 5   | ... | 3·35   | ...                   | 3·555   |
| Oxygen .....          | 5 | ... | 40  | ... | 26·83  | ...                   | 25·205  |
| Nitrogen .....        | 4 | ... | 56  | ... | 37·61  | ...                   | 38·363  |
| <hr/>                 |   |     |     |     |        | <hr/>                 |         |
| Mykomelinic acid .... | 1 |     | 149 |     | 100·00 |                       | 100·000 |

ALLANTURIC ACID.  $C_{10} H_7 O_9 N_4$ . This acid is formed, according to Pelouze, by the action of peroxide of lead and dilute nitric acid, upon uric acid, and upon allantoin: and also when allantoin with water is subjected in a sealed tube to a temperature between  $230^{\circ}$  and  $285^{\circ}$ . It is best obtained by dissolving allantoin in warm nitric acid, separating the nitrate of urea by filtration, and evaporating. The residue is then dissolved in a weak solution of ammonia, and alcohol added to the solution, which throws down *allanturic acid* in the form of a gelatinous precipitate: it must be redissolved in water, and again precipitated by alcohol. It is then white, slightly sour, deliquescent, and almost insoluble in alcohol. By dry distillation it yields hydrocyanic acid, and leaves a bulky residuum. It produces white voluminous precipitates in solutions of nitrate of lead, and nitrate of silver, soluble in excess of acid, as well as of the salt.

HYDURLIC ACID.  $C_{12} H_3 O_9 N_3 + 2HO$ . This acid has been announced by Schlieper as a result of the oxidizement of uric acid by nitric acid; but it has only been once accidentally obtained, and has not been re-examined.



ALLITURIC ACID.  $C_6 H_2 O_3 N_2 + HO$ . Schlieper obtained this acid by boiling a solution of allantoin with excess of hydrochloric acid, down to a small bulk, and treating the residue with nitric acid, which leaves the *allituristic acid* undissolved. It is purified by recrystallization from its solution in boiling water. It forms a crystallizable salt with ammonia, but is decomposed by the action of potassa.

DILITURIC ACID.  $C_8 H O_8 N_3, + HO$ . This acid is found, according to Schlieper, in the nitric solution obtained in the production of the preceding acid, by treating it with sulphuretted hydrogen to remove alloxantine, and filtering. The filtrate, on evaporation, yields yellow lamellar crystals of *diliturate of ammonia*, and parabanic acid. The formula assigned to the diliturate of ammonia is  $NH_4 O, HO, + C_8 H O_8 N_3$ . The dilituric acid itself has not been isolated. It forms explosive salts with potassa, and with oxide of silver.

LEUCOTURIC ACID.  $C_6 H_3 O_6 N_2$ . When an aqueous solution of alloxanic acid is boiled down to the consistence of syrup, and water then added, *leucoturistic acid* remains undissolved, in the form of a white crystalline powder, insoluble in cold, but soluble in boiling water. It is not attacked by the acids; it even resists the action of boiling nitric acid. It is readily soluble in the fixed alkalis, but when those solutions are heated, it is resolved into oxalic acid and ammonia. The *leucoturate of ammonia* crystallizes in long needles: it occasions a white precipitate in solution of nitrate of silver, which is very easily decomposed. The components of this acid are

|                         |   |     |     |     |        |            |
|-------------------------|---|-----|-----|-----|--------|------------|
|                         |   |     |     |     |        | Schlieper. |
| Carbon .....            | 6 | ... | 36  | ... | 31.30  | 31.17      |
| Hydrogen .....          | 3 | ... | 3   | ... | 2.60   | 2.74       |
| Oxygen .....            | 6 | ... | 48  | ... | 41.74  | 41.57      |
| Nitrogen .....          | 2 | ... | 28  | ... | 24.36  | 24.52      |
| <hr/>                   |   |     |     |     |        |            |
| Leucoturistic acid..... | 1 |     | 115 |     | 100.00 | 100.00     |

DIFLUAN.  $C_6 H_4 O_5 N_2$ . This is another product of the decomposition of alloxanic acid, and is contained in the solution which has deposited the leucoturistic acid: this is evaporated to a syrup consistence, and then mixed with a large quantity of alcohol, which occasions a white flocculent precipitate of *difluan*. When dried, it forms a transparent, brittle, gum-like substance, which is deliquescent, and very soluble, and its aqueous solution is not decomposed by boiling. It has a slightly acid reaction, and a pungent, bitter, and saline taste. It produces white precipitates with the salts of lead and silver. It is immediately decomposed by a solution of potassa, evolving ammonia, and producing oxalic acid. Heated with nitric acid, it effervesces, and forms alloxan. Sulphuric acid appears to convert it into oxalic acid and urea. Its ultimate components are the same as those of *murexan*, namely,

|                |   |     |     |     |        |            |
|----------------|---|-----|-----|-----|--------|------------|
|                |   |     |     |     |        | Schlieper. |
| Carbon .....   | 6 | ... | 36  | ... | 33.33  | 32.61      |
| Hydrogen ..... | 4 | ... | 4   | ... | 3.70   | 3.91       |
| Oxygen .....   | 5 | ... | 40  | ... | 37.04  | 37.80      |
| Nitrogen ..... | 2 | ... | 28  | ... | 25.93  | 25.68      |
| <hr/>          |   |     |     |     |        |            |
| Difluan .....  | 1 |     | 108 |     | 100.00 | 100.00     |

**MESOXALIC ACID.**  $C_3O_4 + 2HO$ . 1. When a saturated solution of alloxanate of baryta is boiled, a precipitate falls, consisting of *mesoxalate of baryta*; some carbonic acid is at the same time formed, and urea is found in the liquor. The mesoxalate of baryta which remains dissolved, may be obtained by evaporation. This salt, after having been washed with alcohol, is dissolved in water, the baryta carefully precipitated by sulphuric acid, and the solution gently evaporated: the residue must be purified by recrystallization. 2. When a solution of alloxan is added, drop by drop, to a boiling solution of acetate of lead, a white crystalline precipitate of basic *mesoxalate of lead* falls, which, diffused in water, and decomposed by sulphuretted hydrogen, yields a solution from which, on evaporation, crystallized mesoxalic acid may be obtained.

*Mesoxalic acid* is very sour, and readily soluble in water; it may be boiled and evaporated without change. When neutralized by ammonia, it forms, with the salts of silver, a yellow precipitate, which, on being gently heated, is reduced with effervescence. The components of the *mesoxalate of lead* are, according to Liebig,  $2PbO, + C_3O_4$ , so that, in its formation, 1 atom of urea appears to be abstracted from 1 atom of alloxan, so as to leave 2 atoms of mesoxalic acid.

|                           |                   |
|---------------------------|-------------------|
| 1 atom of alloxan .....   | $C_8H_4O_{10}N_2$ |
| –1 „ urea .....           | $C_2H_4O_2N_2$    |
| <hr/>                     |                   |
| =2 „ mesoxalic acid ..... | $C_6O_8$          |

The *mesoxalate of baryta* is probably  $BaO, HO, C_3O_4$ . (LIEBIG.)

**PARABANIC ACID.**  $C_6H_2O_6N_2 = C_6O_4N_2 + 2HO$ . (LIEBIG and WÖHLER.) This acid is prepared by dissolving 1 part of uric acid, or of alloxan, in 8 parts of moderately strong nitric acid, evaporating to the consistence of syrup, and setting aside to crystallize. The first crop of crystals require purification by a second or third solution and recrystallization. It may also be obtained from the mother-liquor of the preparation of alloxan by Gregory's process, if it be gently heated with an additional quantity of nitric acid.

*Parabanic acid* forms colorless, transparent, 6-sided prisms, of a very sour taste, very soluble in water, and permanent in the air. When heated, it fuses, and partly sublimes unchanged; a part of it is at the same time decomposed into hydrocyanic acid. The aqueous solution of this acid may be boiled, even with the stronger acids, without decomposition. A cold solution of parabanic acid, neutralized by ammonia, produces a white precipitate in a solution of nitrate of silver. When solutions of the salts of parabanic acid are heated, they pass into *oxalates*.

Parabanic acid is formed by the decomposition of 1 atom of uric acid, which, by the addition of 2 atoms of water, and 4 of oxygen derived from the nitric acid, is resolved into 2 atoms of carbonic acid, 1 of parabanic acid, and 1 of urea: the latter is decomposed by the hypochlorous acid (see p. 1813). The components of the *hydrated parabanic acid* are,



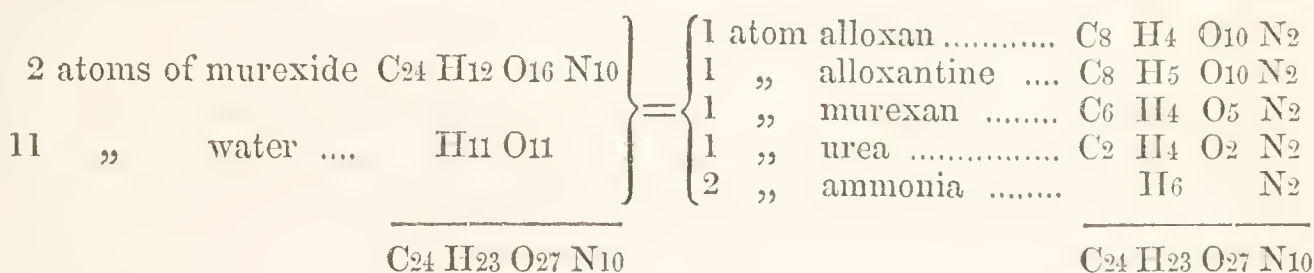
|                                    |   |     |     |     | Liebig and<br>Wöhler. |     |        |                            |   |     |     |     |        |
|------------------------------------|---|-----|-----|-----|-----------------------|-----|--------|----------------------------|---|-----|-----|-----|--------|
| Carbon .....                       | 6 | ... | 36  | ... | 31·58                 | ... | 31·84  | Anhydrous }<br>acid..... } | 1 | ... | 96  | ... | 84·21  |
| Hydrogen .....                     | 2 | ... | 2   | ... | 1·75                  | ... | 1·82   |                            |   |     |     |     |        |
| Oxygen .....                       | 6 | ... | 48  | ... | 42·10                 | ... | 41·80  |                            |   |     |     |     |        |
| Nitrogen.....                      | 2 | ... | 28  | ... | 24·57                 | ... | 24·54  |                            |   |     |     |     |        |
| <hr/>                              |   |     |     |     |                       |     |        |                            |   |     |     |     |        |
| Hydrated parabanic }<br>acid ..... | 1 |     | 114 |     | 100·00                |     | 100·00 |                            | 1 |     | 114 |     | 100·00 |

MUREXIDE.  $C_{12}H_6O_8N_5$ . *Purpurate of ammonia* of Prout. This beautiful and curious product of the decomposition of uric acid may be obtained in several ways. 1. A mixture of 1 part of dry uramile, 1 part of red oxide of mercury, and 40 parts of water, to which a few drops of ammonia are added, is boiled till the mixture acquires a deep purple tint; it is then filtered whilst boiling hot, and, as it cools, it deposits crystals of pure murexide. 2. Seven parts of hydrated alloxan and 4 of alloxantine are dissolved together in 240 parts of boiling water, and the solution added to 80 parts of a cold but saturated solution of sesquicarbonate of ammonia; the mixture instantly acquires a magnificent purple color, and effervescence ensues from the escape of carbonic acid; as soon as it cools, an abundant crystalline deposit of murexide ensues; it may be collected upon a filter, washed with a little cold water, and dried. The finest crystals are obtained by operating upon a small scale, as by using 4 grains of alloxan, 7 of alloxantine, dissolved by boiling in half an ounce of water, and adding the hot solution to one-sixth of an ounce by measure of a cold saturated solution of carbonate of ammonia; this mixture has exactly the proper temperature for the formation of murexide, and does not, owing to its small bulk, remain too long hot. Dr. Gregory, to whom we are indebted for these directions, observes, that if we do not care about having the finest crystals, we may prepare murexide in large quantity, by adding solution of alloxan to a boiling solution of alloxantine, and cautiously adding cold solution of carbonate of ammonia till the mixture has become nearly black, and the green crystals begin to appear. The vessel being removed from the fire, a large quantity of murexide is deposited. In these processes, the residual liquid is still colored, and is alkaline from excess of ammonia; if kept, it loses its red color, and when evaporated, yields crystals of alloxanate of ammonia. (*Outlines of Chemistry*, p. 327.)

*Murexide* forms small short four-sided prisms, which are deep red by transmitted light, but green and iridescent by reflected light. They form a beautiful object for the microscope. Their powder is red, but acquires a metallic green lustre under the burnisher. This substance is very sparingly soluble in cold water, producing a purple solution; it dissolves copiously in boiling water, but is insoluble in alcohol and in ether, and only slightly soluble in a saturated solution of carbonate of ammonia. The composition of murexide has not, perhaps, been very accurately determined, and there are different views of its constitution; the result of the analysis of Liebig and Wöhler, however, which has been verified by other experimentalists, closely agrees with the formula given above; namely,

|                |    |       |     |       |        | Wöhler and<br>Liebig. |
|----------------|----|-------|-----|-------|--------|-----------------------|
| Carbon.....    | 12 | ..... | 72  | ..... | 33·96  | ..... 34·093          |
| Hydrogen ..... | 6  | ..... | 6   | ..... | 2·83   | ..... 3·000           |
| Oxygen .....   | 8  | ..... | 64  | ..... | 30·18  | ..... 30·094          |
| Nitrogen ..... | 5  | ..... | 70  | ..... | 33·03  | ..... 32·813          |
| <hr/>          |    |       |     |       |        |                       |
| Murexide.....  | 1  |       | 212 |       | 100·00 | ..... 100·000         |

Murexide is decomposed when long boiled with water. When its solution in boiling water is mixed with dilute hydrochloric or sulphuric acid, crystals of *murexan* are deposited, and ammonia, alloxan, alloxantine, and urea, are retained in solution. This decomposition may be represented as follows (LÖWIG. *Chem. der Organ. Verbind.*, ii. 1524):

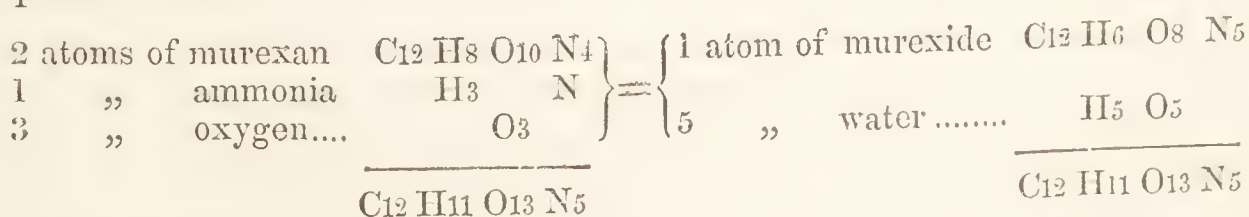


When sulphuretted hydrogen is passed through a concentrated solution of murexide, it is immediately decolored, crystals of *murexan* are formed, and alloxantine and ammonia are found in the liquor. The products of the decomposition of murexide by the alkalis, as well as by other agents, are very complicated, and have given rise to various opinions connected with its formula, and respecting which many points are still undetermined. (See GREGORY. *Outlines*, p. 328.)

MUREXAN.  $C_6 H_4 O_5 N_2$ . *Purpuric acid* of Prout. When this substance is precipitated from an alkaline solution of murexide, by an acid, it forms a light shining powder, soluble without decomposition in sulphuric acid. It has no acid characters, for, although it dissolves in the alkalis, it does not saturate or neutralize them. Its components, according to the analyses of Wöhler and Liebig, are

|                |   |      |     |      |        | Liebig and<br>Wöhler. |
|----------------|---|------|-----|------|--------|-----------------------|
| Carbon.....    | 6 | .... | 36  | .... | 33·33  | .... 33·614           |
| Hydrogen ..... | 4 | .... | 4   | .... | 3·70   | .... 3·711            |
| Oxygen .....   | 5 | .... | 40  | .... | 37·04  | .... 36·952           |
| Nitrogen.....  | 2 | .... | 28  | .... | 25·93  | .... 25·723           |
| <hr/>          |   |      |     |      |        |                       |
| Murexan .....  | 1 |      | 108 |      | 100·00 | ..... 100·000         |

A solution of murexan in aqueous ammonia is at first colorless, but on exposure to air it absorbs oxygen, and becomes red, and at length it deposits murexide.



Hence murexide is produced from murexan, in the same way as orcéine from oricine, and phloridzéine from phloridzine.

Prout, who discovered murexide, regarded it as a compound of  $6 C 2$



ammonia and a peculiar acid which he called *purpuric acid*, and which might be separated by other acids. But, according to Liebig and Wöhler, purpuric acid and ammonia cannot reproduce murexide in the absence of oxygen; and when purpuric acid is separated, other products are at the same time formed; they are therefore inclined to regard murexide as a peculiar amide-like compound. But Fritzsche considers murexide as a true salt of ammonia, the acid of which, though it cannot be isolated, may be transferred by double decomposition, to other bases, with which it generally forms difficultly-soluble salts, many of which have a purple color. According to Fritzsche the purpuric acid, as it exists combined with bases, is  $C_{16}H_4O_{10}N_5$ ; and murexide (purpurate of ammonia) is  $NH_4O, C_{16}H_4O_{10}N_5$ . Fritzsche has described and analysed several of the *purpurates*, with results consistent with these views. (LÖWIG, ii. 1526.)

COMPOSITION OF URINE IN DISEASES. The urine is liable to infinite modifications both in the quantity and quality of its components, and when these deviations from a healthy standard are regular or constant, or when they exceed certain limits, they constitute *morbid states* of the secretion.

I have already adverted to the new characters which the urine sometimes acquires from particular kinds of food or medicine. Odorous principles are often carried off by it, as in the case of asparagus, oil of turpentine, and several other varieties of volatile oil. During a course of mercurial friction, mercury is said to have been found in the sediment, which, in such cases, is generally deposited; and traces of iron have been found during a course of chalybeate remedies. Nitre, ferrocyanide, and sulpho-cyanide of potassium, iodine, and iodic salts, several borates, carbonates, chlorates, and even silicates, and many of the acids and alkalis, have also been traced passing off from the stomach by the kidneys; some of the vegetable salts with alkaline bases appear to suffer such decomposition, as to act upon the urine in the manner of free alkalis, the acid being decomposed. Among the substances which pass off by urine, none are more remarkable, or more easily observed, than certain coloring-matters of vegetable origin, such as those of many fruits, logwood, madder, rhubarb, and also several astringents; these sometimes are not apparent, till the urine is tested by an alkali, or by solution of iron. The mineral acids, alcohol, ether, camphor, empyreumatic oils, musk, the coloring-matters of cochineal, litmus, and *sap-green* (which is the green extractive of the *Rhamnus catharticus*) and others, insoluble in water, are said not to pass by urine in an unchanged state. According to Landerer (*Chem. Gaz.*, January, 1843), quinia not only passes off by urine, but is also found in the blood and excrements. (See p. 1435.)

In many diseases, there is an excessive secretion of *acid* along with the urine; this is sometimes *uric acid*, which we shall presently refer to, and sometimes oxalic or even nitric acid, neither of which belong to healthy urine; I have also observed a peculiar acid state of urine depending upon a volatile acid, which I believe to be either the acetic or lactic. In a case of *chorea*, Pettenkofer found the urine loaded with hippuric acid. Nor is an *alkaline* state of urine, or at least a deficiency in the proper proportion of acid, at all uncommon; it is often the result of particular food and medicine, and sometimes habitual; in such cases, the urine has a tendency to a white deposit, or film; and is usually

opalescent, when voided, or speedily becomes so. This is generally the case in injuries of the spine affecting the nerves which supply the kidneys, and in these cases ammoniacal urine is sometimes voided. There are many other causes affecting the prevalence of the *phosphates* in the urine, respecting which some valuable information will be found in Dr. Bence Jones's communications to the Royal Society. (*Phil. Trans.*, 1845, p. 335; and 1846, p. 449.) During pregnancy the urine is stated to be less acid than usual, and even sometimes alkaline; the salts of lime are also in smaller quantity, a circumstance connected, it is supposed, with the formation of foetal bone. (*Chem. Gaz.*, December, 1842.)

The relative proportion of *urea* fluctuates on one side or other of the healthy standard, from a variety of causes: when it is defective, the urine loses its putrefactive tendency, and there is not that production of ammonia which belongs to healthy urine. In inflammatory affections of the liver, in hysteria, in some cases of excessive secretion of albuminous matter, and in some of diabetes, there is this deficiency of *urea*. In other cases, *urea* is in excess, so that nitric acid added to the urine causes a deposition of nitrate of *urea*. Dr. Prout judges of the presence of excess of *urea*, by putting the urine into a watch-glass, and dropping in a little nitric acid, so as to collect at the bottom; if there be a separation of crystals of nitrate of *urea* in the course of less than half an hour, that ingredient is probably present in morbid proportion.

*Albumine*, or some modification of it, which is a common ingredient in healthy urine, but always in very small relative proportion, is so abundant in some cases of disease, as to coagulate by heat, or even sometimes spontaneously within the bladder. *Albumine* is recognised by the precipitate which it affords to ferrocyanide of potassium; but in applying this test, and, indeed, generally, in judging of the state of the urine of any individual, it should be previously ascertained that it is not naturally or habitually subject, (which is at times the case,) to excess or deficiency of this, or others of its components. In some forms of dropsy, especially where there is renal disease, excess of *albumine* is often observed; in these instances the urine is scanty, and its specific gravity below the usual average, in consequence of deficiency in saline matter and in *urea*; and it deserves notice, that in some such cases, *urea* exists in the blood.

According to Dumas traces of *fat* may always be found in healthy urine, but in certain diseases, and especially in phthisis, it may so far increase, as to be perceptible floating upon the surface. Where there is excess of *fat* in the serum of the blood, the urine, according to Dumas, assumes more or less of a milky aspect, arising from *albumine*; this he terms *chylous urine*. Some have suspected the presence of *milk* in urine, in such cases.

A peculiar *red* coloring matter, differing from any uric or purpuric combination, is sometimes present in the urine, associated with the lateritious sediment; it is soluble in alcohol; but it has not been accurately examined. Messrs. Brett and Bird have adverted to such cases in a paper published in the *Medical Gazette*, for August, 1834. A *blue* and *black* coloring matter have been observed in the urine, but they are of very rare occurrence; the former is the *cyanurine* of Braconnot; the latter has been noticed by Proust. (*Ann. Ch. et Ph.*, xiv. 264.) These appear to be peculiar organic compounds; the former has been mistaken for Prussian blue. The yellow, brown, or green tint, which urine some-



times acquires in jaundice and obstructions of the liver, seems to depend upon the presence of *bile*, or of its coloring matter. In these cases, hydrochloric acid brightens the color, or renders it green.

The most extraordinary morbid change which urine suffers is that connected with the formation of *sugar* in the disease called *diabetes*. This urine does not easily putrefy, and may be made to undergo vinous fermentation; it is usually of a pale color, and more or less sweet to the taste, and its specific gravity is commonly above the healthy standard\*; it is not, as is often supposed, destitute of, and even generally, I believe, not deficient in, urea. The presence of sugar in the urine is indicated by its tendency to ferment when in a warm place, especially on the addition of a little yeast: the influence of sugar upon certain salts of copper (p. 1188) may also be made available, as a test, in these cases: a few drops of solution of sulphate of copper added to healthy urine occasions a slight blue cloud of phosphate of copper, and on adding a little potassa, hydrated oxide of copper is thrown down, which, if sugar be present, is redissolved by excess of potassa, forming a deep blue solution; and on heating the solution, the copper falls in the state of red suboxide: if there be no sugar, the black oxide only is formed. (GOLDING BIRD, *Lond. Med. Gaz.*, 1843; *Pharm. Journ.*, January, 1844.)

*Diabetic Sugar* may be obtained by evaporating such urine to the consistency of syrup, and keeping it in a warm place, when a granular mass is obtained which must be washed with cold alcohol to abstract the coloring matter; it may then be dissolved in boiling alcohol, and purified

\* The following table, constructed by Dr. Henry, shows the quantity of solid extract, in a wine-pint of urine of different specific gravities, from 1·020, to 1·050. In the experiments which furnished the data of this table, the urine was evaporated by a steam-heat till it ceased to lose weight, and left an extract which became

solid on cooling. (*Med.-Chir. Trans.*, ii. 118.) This is a useful table to the medical practitioner, who, in cases of diabetes, may draw important inferences respecting the progress of the disease, and the influence of medicines, from the differing density of the urine.

| Specificgravity compared with 1000 parts of water at 60°. | Quantity of solid extract in a wine pint. | Quantity of solid extract in a wine-pint, in | Specificgravity compared with 1000 parts of water at 60°. | Quantity of solid extract in a wine-pint. | Quantity of solid extract in a wine-pint, in |
|---|---|--|---|---|--|
|   | grs.                                      | oz. dr. scr. grs.                            |   | grs.                                      | oz. dr. scr. grs.                            |
| 1020  | 382·4                                     | 0 6 1 2                                      | 1036  | 689·6                                     | 1 3 1 9                                      |
| 1021  | 401·6                                     | 0 6 2 1                                      | 1037  | 708·8                                     | 1 3 2 8                                      |
| 1022  | 420·8                                     | 0 7 0 0                                      | 1038  | 728·0                                     | 1 4 0 8                                      |
| 1023  | 440·0                                     | 0 7 1 0                                      | 1039  | 747·2                                     | 1 4 1 7                                      |
| 1024  | 459·2                                     | 0 7 1 19                                     | 1040  | 766·4                                     | 1 4 2 6                                      |
| 1025  | 478·4                                     | 0 7 2 18                                     | 1041  | 785·6                                     | 1 5 0 5                                      |
| 1026  | 497·6                                     | 1 0 0 17                                     | 1042  | 804·8                                     | 1 5 1 4                                      |
| 1027  | 516·8                                     | 1 0 1 16                                     | 1043  | 824·0                                     | 1 5 2 3                                      |
| 1028  | 536·0                                     | 1 0 2 16                                     | 1044  | 843·2                                     | 1 6 0 3                                      |
| 1029  | 555·2                                     | 1 1 0 15                                     | 1045  | 862·4                                     | 1 6 1 2                                      |
| 1030  | 574·4                                     | 1 1 1 14                                     | 1046  | 881·6                                     | 1 6 2 1                                      |
| 1031  | 593·6                                     | 1 1 2 13                                     | 1047  | 900·8                                     | 1 7 0 0                                      |
| 1032  | 612·8                                     | 1 2 0 12                                     | 1048  | 920·0                                     | 1 7 1 0                                      |
| 1033  | 632·0                                     | 1 2 1 12                                     | 1049  | 939·2                                     | 1 7 1 19                                     |
| 1034  | 651·2                                     | 1 2 2 11                                     | 1050  | 958·4                                     | 1 7 2 18                                     |
| 1035  | 670·4                                     | 1 3 0 10                                     |   |   |  |

by repeated solution and crystallization, or by the help of animal charcoal. It is a granular sugar, resembling grape sugar in appearance and composition. (See *granular sugar*, p. 1184.)

The following analyses of diabetic urine are by Meisner; the different samples were taken at different periods from the same individual.

|  | I.         | II.        | III.  |
|--|------------|------------|-------|
| Substances soluble in ether: urea, lactic acid, }<br>lactate of lime, extractive ..... | 0·34 ....  | 0·33 ....  | 0·65  |
| Substances soluble in alcohol: sugar, extrac- }<br>tive, salts .....                   | 7·06 ....  | 3·46 ....  | 5·78  |
| Substances soluble in water: extractive, salts   | 1·37 ....  | 3·44 ....  | 0·99  |
| Mucus, with phosphate of lime and traces of }<br>oxide of iron .....                   | 0·34 ....  | 0·31 ....  | 0·46  |
| Water' .....   | 91·19 .... | 92·46 .... | 92·10 |

Simon, and Bouchardat, have also analyzed diabetic urine, with the following results. (DUMAS, *Chim. App. aux Arts.*, viii. 557.)

|                                | Simon.        |              | Bouchardat. |
|--------------------------------|---------------|--------------|-------------|
| Sp. gr. ....                   | (1·018) ..... | (1·016)      |             |
| Water .....                    | 957·00 .....  | 960·00 ..... | 837·58      |
| Solid contents .....           | 43·00 .....   | 40·00 .....  | 162·42      |
| Urea .....                     | traces .....  | 7·99 .....   | 8·27        |
| Uric acid .....                | traces .....  | traces       |             |
| Sugar .....                    | 39·80 .....   | 25·00 .....  | 134·42      |
| Alcoholic extract .... } ..... |               |              | 6·38        |
| Aqueous extract .... } .....   | 2·10 .....    | 6·50 .....   | 5·27        |
| Salts .....                    |               |              | 8·69        |
| Phosphates and mucus .....     | 0·52 .....    | 0·30 .....   | 0·24        |
| Albumine .....                 | traces .....  | traces       |             |
| Oxide of iron ? .....          |               |              | 0·14        |

According to Bouchardat, sugar may be found in the blood of diabetic patients, if examined shortly after meals: he refers its formation, to the amylaceous elements of the food, and regards a strict adherence to animal diet as always effecting a diminution of the saccharine contents of the urine: he suggests, in these cases, the use of a bread composed exclusively of gluten, and entire abstinence from all forms of starch, sugar, and gum.

In *diabetes insipidus*, the urine, though not sweet, is excessive in quantity, and deranged as to composition; the formation of urea is suspended; and such urine leaves, on evaporation, a brown residue, of the consistence of syrup, from which nothing crystallizes, and which is slightly acid. Alcohol of ·830 dissolves the greater part of this residue, and leaves, on evaporation, a yellow, deliquescent extractive matter, which resembles that which similar alcohol extracts from the inspissated decoction of muscular flesh. The portion insoluble in alcohol appears also to partake of the same properties. (BERZELIUS.)

**CALCULOUS CONCRETIONS.** It frequently happens that certain ingredients in the urine are secreted in excess, or that, from other causes, they are deposited in a solid form, constituting *sand*, *gravel*, and *calculi*.

Sabulous depositions in the urine are of various characters, but, as far as their leading chemical varieties are concerned, they may be conveniently termed *white sand* and *red sand*; the former consisting



usually of *phosphate of lime*, or *ammonio-magnesian phosphate*, or of mixtures of the two; whilst in the latter, *uric acid* predominates. These deposits are frequently temporary only, and may be produced by a variety of accidental causes, which influence the secretion of urine; but when they are more or less constant, or arise from very trifling causes, they then require the utmost attention, as being frequent forerunners of calculus. This tendency to the deposition of solid matter is generally first observed in the urine after it is voided, and as it cools; but it afterwards increases to such an extent, that it is voided more or less turbid; and, at length, symptoms of gravel, or of stone in the kidney or bladder ensue.

*Urinary calculi* are composed either of materials that exist at all times in the urine, or of substances which only occasionally appear, and which may, therefore, be regarded as products of disease. The following are their principal component ingredients:—

- |                                 |                       |
|---------------------------------|-----------------------|
| 1. Uric acid.                   | 6. Cystic oxide.      |
| 2. Urate of ammonia.            | 7. Carbonate of lime. |
| 3. Phosphate of lime.           | 8. Xanthic oxide.     |
| 4. Ammonio-magnesian phosphate. | 9. Silica.            |
| 5. Oxalate of lime.             |                       |

Of these substances, the first five are of most frequent occurrence, but their relative frequency varies in different countries and districts. Dr. Yelloly, in a paper on the “Tendency to Calculous Diseases,” (*Phil. Trans.*, 1829,) has given the following view of the different descriptions of calculi contained in the collection belonging to the Norwich hospital: from this table it will be seen that about one-half of the specimens are composed of one description of material only; and that the remainder consist of alternating layers, more or less numerous, of most of the substances of which human urinary calculi are composed.

*Calculi consisting principally of one deposit.*

|   |    |
|---|----|
| Lithic (or uric) acid .....   | 81 |
| Lithate of ammonia.....   | 20 |
| Oxalate of lime .....   | 20 |
| Phosphate of lime .....   | 4  |
| Fusible calculus, or mixed phosphates; that is to say, calculi composed of the triple, or ammoniaco-magnesian phosphate, mixed with phosphate of lime ..... | 37 |

*Calculi consisting of two deposits.*

|  |    |
|--|----|
| Lithic acid and lithate of ammonia .....     | 37 |
| „ oxalate of lime .....                      | 11 |
| „ mixed phosphates .....                     | 10 |
| „ phosphate of lime .....                    | 2  |
| Lithate of ammonia and lithic acid .....     | 2  |
| „ oxalate of lime .....                      | 25 |
| „ mixed phosphates .....                     | 14 |
| „ phosphate of lime .....                    | 1  |
| Oxalate of lime and lithic acid .....        | 10 |
| „ lithate of ammonia.....                    | 1  |
| „ mixed phosphates .....                     | 15 |
| „ phosphate of lime .....                    | 3  |
| Mixed phosphates and phosphate of lime ..... | 2  |

*Calculi consisting of three deposits.*

|   |   |
|---|---|
| Lithic acid, phosphate of lime, and mixed phosphates .....      | 2 |
| „ oxalate of lime, and phosphate of lime .....                  | 1 |
| „ oxalate of lime, and lithate of ammonia .....                 | 2 |
| „ oxalate of lime, and lithic acid .....                        | 4 |
| „ lithate of ammonia, and oxalate of lime.....                  | 2 |
| „ oxalate of lime, and mixed phosphates .....                   | 1 |
| Lithate of ammonia, oxalate of lime, and mixed phosphates ..... | 3 |
| „ oxalate of lime, and lithic acid.....                         | 8 |
| „ phosphate of lime, and lithate of ammonia.....                | 1 |
| „ lithic acid, and mixed phosphates .....                       | 2 |
| Oxalate of lime, lithic acid, and lithate of ammonia.....       | 1 |
| „ lithic acid, and oxalate of lime .....                        | 1 |
| „ lithic acid, and mixed phosphates .....                       | 2 |

*Calculi consisting of four or more deposits.*

|   |       |
|---|-------|
| Lithate of ammonia, oxalate of lime, lithic acid, and mixed phosphates                                | 1     |
| Oxalate of lime, lithic acid, oxalate of lime, and mixed phosphates....                               | 1     |
| Lithate of ammonia, oxalate of lime, phosphate of lime, oxalate of lime, and lithate of ammonia ..... | 1     |
|   | <hr/> |
|   | 328   |

In the last edition of Dr. Prout's work *On the Nature and Treatment of Stomach and Urinary Diseases*, there is a table in which the urinary calculi contained in the museums of Bartholomew's and Guy's hospitals, and in the provincial hospitals of Norwich, Manchester, and Bristol, are contrasted with the calculi existing in Swabia and Copenhagen; this table is interesting, as showing the relative prevalence of the different species of calculi, and the order of succession of their different layers.

The following are the distinctive characters of the principal varieties of urinary calculi.

1. *Calculi composed of uric acid*, the chemical properties of which have already been described, are of a brown or fawn color; and, when cut through, appear of a more or less distinctly laminated texture. Their surface is generally smooth, or nearly so, being sometimes slightly tuberculated. Before the blowpipe, this calculus blackens, and gives out a peculiar ammoniacal odor, leaving a minute portion of white ash: it is soluble in solution of pure potassa, and, heated with a little nitric acid, it affords the red compound above-mentioned.

2. *Urate of ammonia* forms calculi, the surface of which is sometimes smooth, sometimes tuberculated: they are made up of concentric layers, and the fracture is fine earthy, resembling that of compact limestone; they are generally of a small size, and rather uncommon, though urate of ammonia often occurs mixed with uric acid. It usually decrepitates before the blowpipe, evolves ammonia when heated with solution of potassa, and is somewhat more soluble in solutions of caustic potassa, or soda, than pure uric acid.

3. *Phosphate of lime calculus* is of a pale-brown or gray color, smooth, and made up of regular and easily separable laminæ. It is soluble in hydrochloric acid, and precipitated by pure ammonia, and does not fuse before the blowpipe. *Calculi from the prostate gland* are frequently composed of phosphate of lime.



4. *Ammonio-magnesian*, or *triple calculus*, is generally white, or pale-gray, and the surface often presents minute crystals; its texture is generally compact, and often somewhat hard and translucent; heated by the blowpipe, it exhales ammonia, and leaves phosphate of magnesia. It is more easily soluble than the preceding; and oxalate of ammonia forms no precipitate in its hydrochloric solution.

It frequently happens that calculi consist of a mixture of the two last-mentioned substances, in which case they fuse before the blowpipe, and are hence termed *fusible calculi*. They are white, or nearly so, and softer than the separate substances, often resembling chalk in appearance. They are easily soluble in hydrochloric acid, and if oxalate of ammonia be added to their solution, the lime is precipitated in the state of oxalate.

5. *Oxalate of lime* forms calculi, the exterior color of which is generally dark-brown, or reddish; they are commonly rough, or tuberculated upon the surface, and have hence been called *mulberry calculi*. Before the blowpipe, they blacken and swell, leaving a white infusible residue, which is easily recognised as quicklime. Small oxalate of lime calculi are, however, sometimes perfectly smooth upon the surface, and somewhat resemble a hempseed in appearance.

6. *Cystine*, or *cystic oxide*.  $C_6 H_6 O_4 N S_2$ . This curious substance was discovered by Wollaston (*Phil. Trans.*, 1810, p. 223); it has hitherto only been found in human urinary concretions, and is of rare occurrence. The calculi composed of it are in appearance most like those of the ammonio-magnesian phosphate. They are soft, and when burned by the blowpipe, exhale a peculiar foetid odor. They are soluble in nitric, sulphuric, hydrochloric, phosphoric, and oxalic acids, and also in alkaline solutions. Cystine forms crystallizable compounds with nitric, hydrochloric, and oxalic acids. With sulphuric acid it forms a viscid, colorless, and uncrystallizable compound. When cystine is boiled with baryta-water, sulphuret of barium is formed, and a yellow shining substance, soluble in water, and of an alliaceous odor, is deposited; it contains sulphur and nitrogen. A solution of cystine in hydrochloric acid, yields, when evaporated *in vacuo*, crystals composed of 2 atoms of cystine and 1 of the acid: it also combines with nitric acid.

Cystine has been analysed by Prout, by Thaulow (*Ann. der Pharm.*, xxvii. 197), and by Baudrimont and Malaguti. (*Journ. de Pharm.*, xxiv. 633.) Its components are,

|                |   |     |     |       |        | Thaulow. | Prout. |
|----------------|---|-----|-----|-------|--------|----------|--------|
| Carbon .....   | 6 | ... | 36  | ...   | 30.00  | 30.31    | 29.87  |
| Hydrogen ..... | 6 | ... | 6   | ...   | 5.00   | 5.10     | 5.12   |
| Oxygen .....   | 4 | ... | 32  | ...   | 26.66  | 28.38    | 53.15  |
| Sulphur .....  | 2 | ... | 32  | ...   | 26.66  | 25.21    |        |
| Nitrogen ..... | 1 | ... | 14  | ...   | 11.68  | 11.00    | 11.86  |
| <hr/>          |   |     |     | <hr/> |        |          |        |
| Cystine .....  | 1 |     | 120 |       | 100.00 | 100.00   | 100.00 |

Lassaigne has described a calculus from the bladder of a dog, under the name of *cystic oxide* (*Ann. Ch. et Ph.*, xxii. 329), which is altogether of different composition: it afforded 36.2 carbon, 12.8 hydrogen, 17 oxygen, and 34 nitrogen, *per cent*.

7. Dr. Prout, and Mr. Smith of Bristol, (*Medico-Chir. Trans.*, xi. 14,) have described calculi composed almost entirely of *carbonate of lime*;

but this species is exceedingly rare, and among several hundred calculi which I have examined, I never met with it from the human bladder. Carbonate of lime calculi are small, white, and friable. I have seen many beautiful specimens of carbonate of lime calculus from other animals. I have also observed very small and perfectly spherical concretions, composed of carbonate of lime and animal matter, voided in a case in which they apparently came from the prostate gland. In the case of this calculus cited by Mr. Smith, several small ones were voided, and three large calculi of similar composition were removed by operation.

8. *Xanthic Oxide. Xanthine. Uric Oxide.*  $C_5H_2O_2N_2$ . This substance has already been adverted to as discovered in a calculus by Dr. Marcet; Dr. Prout observes that he has never met with another specimen. "Some late writers," he observes, "assert that xanthic oxide forms a constituent of certain lithic acid calculi of a light or bright brown color, and which exhibit a scaly shining fracture of a brown or deep flesh-color, and yield a resinous lustre by friction. I cannot confirm or deny this statement." To obtain *xanthic oxide* Liebig directs us to dissolve the calculi containing it in caustic potassa, and saturate the solution with carbonic acid, which, he says, throws down xanthic oxide in the form of a white precipitate, which becomes hard and yellow by drying, and acquires a waxy lustre by friction. It is soluble in the pure and carbonated alkalis, but sparingly soluble in hot water and in hydrochloric and oxalic acids. It forms a deep yellow solution with concentrated sulphuric acid, which is not precipitated by water. Nitric acid dissolves it without effervescence, and on evaporation there remains a residue which is not reddened by ammonia, but is of a *lemon-yellow* color, and little soluble in water; the alkalis dissolve this residue, becoming deep yellow, and leave a residuum of a red color on evaporation. Liebig observes that the calculi containing xanthic oxide are of cinnamon color, and have a smooth surface, a lamellar fracture, and a waxy appearance when rubbed. He assigns to this substance the above formula. Other chemists have hitherto failed in detecting it\*.

9. *Silica*, as an ingredient in urinary sand, and in some calculi, is very rare. It would appear from the statement of Venables (*Quart. Journ.*, N.S., December, 1829), that it most commonly is voided in the form of sand. Several supposed cases of silicious sand have been traced to imposture. I have, however, seen, in the possession of Dr. Yelloly, an unequivocal specimen of siliciferous calculus; it was taken from a boy by an operation, and consisted chiefly of oxalate of lime, having small cavities in its interior, lined with an apparently chalcedonic crust, which, on examination, proved to be silica.

These are the principal chemical facts belonging to the history of urinary calculi. In Dr. Wollaston's valuable papers upon this subject, (*Phil. Trans.*, 1797 and 1810,) much additional information will be found. In the same work (1806, 1808, and 1810), I have given some

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\* Unger obtained a substance from Peruvian guano, which at first he regarded as identical with xanthic oxide: he represents it as a basic substance, and describes several of its combinations: it has been designated *guanine*, and the formula  $C_{10}H_5O_2N_5$ , has been assigned to it. It appears to require further examination. (*Poggend. Ann.*, LXV. 222. *Ann. der Pharm.*, LVIII. 18, and LIX. 58.)



account of their peculiarities, depending upon their situation, and of the chemical operation of *solvents*, a subject taken up more in detail in the *Quarterly Journal of Science and the Arts*, vol. iii. Marcet published a valuable dissertation on *Calculous Disorders*: but Prout's "Inquiry into the Nature and Treatment of Gravel, Calculus," &c., is the most complete medico-chemical work upon the subject.

**URINE OF OTHER ANIMALS.** From comparative analyses of the urine of different animals, it appears that *urea* is always present in the higher orders. The urine of *carnivorous animals* is at first acid, but becomes speedily alkaline, and is very prone to putrefaction; it generally contains uric acid, but in small quantity. The urine of *graminivorous animals* contains *hippuric acid*, which acid becomes benzoic acid when the urine is evaporated at  $212^{\circ}$ . According to Hieronymi, as quoted by Berzelius, the urine of the *lion*, *tiger*, and *leopard*, is transparent, and of a nauseous odor and bitter taste; its specific gravity varies in the same individual, from 1.059 to 1.076. As soon as voided, it becomes alkaline from the formation of carbonate of ammonia. During evaporation it deposits white flakes; and when concentrated, part of the urea crystallizes. The urine of the tiger yielded

|  |               |
|--|---------------|
| Urea, extractive, and free acetic (lactic ?) acid.....                       | 13.220        |
| Uric acid.....   | 0.022         |
| Mucus.....   | 0.510         |
| Sulphate of potassa.....   | 0.122         |
| Hydrochlorate of ammonia, and chloride of sodium .....                       | 0.116         |
| Phosphate of lime and magnesia, with a trace of carbonate }<br>of lime ..... | 0.176         |
| Phosphate of potassa and of soda .....                                       | 0.802         |
| Phosphate of ammonia .....   | 0.102         |
| Acetate (lactate) of potassa .....   | 0.330         |
| Water.....   | 84.600        |
|  | <hr/> 100.000 |

The urine of the *hyæna* and *panther* contained the same ingredients, the specific gravity of the former being 1.061, and of the latter, 1.045.

The urine of the *rhinoceros* is muddy, yellow, and, when exposed to air, acquires a crystalline film of carbonate of lime; it effervesces and becomes clear on the addition of an acid. Left to itself, it deposits a yellow powder, composed of carbonate of lime and magnesia, traces of oxide of iron, of silica, and of an azotized animal matter; the clear portion, when evaporated, yields a similar precipitate, and on the addition of hydrochloric acid, deposits *urobenzoic acid*. (VOGEL.)

*Elephant's urine* is turbid from carbonate of lime and magnesia; it contains no *benzoate*, but much urea. (VOGEL.)

The urine of the *horse* contains urea 0.7, hippurate of soda 2.4, carbonate of soda 0.9, chloride of potassium 0.9, carbonate of lime 0.2 to 1.1, water 94.0. Chevreul found sulphate of lime.

The urine of the *camel* yielded carbonate of ammonia and volatile oil by distillation; sulphuric, nitric, and hydrochloric acid, reddened it: on evaporation it deposited carbonate of lime and of magnesia, with animal matter and a trace of silica. Evaporated to the consistence of syrup, and mixed with nitric acid, it deposited abundance of nitrate of urea.

It also contained chloride of sodium, hippurate of soda, carbonate of soda, sulphate of potassa in large proportion, some sulphate of soda, and carbonate of ammonia, and a trace of oxide of iron. No phosphoric salts or uric acid. (CHEVREUL.) I found a trace of uric acid in camel's urine. (*Phil. Trans.*, 1806, p. 376.)

The urine of the *cow* contains a large relative proportion of urea and of hippuric acid, and exposed to air, deposits small crystals of carbonate of lime and carbonate of magnesia. When fresh it is transparent, amber-colored, of a peculiar and not disagreeable odor, and neutral to test papers: its specific gravity, owing chiefly to its abundance of urea, is 1.0325.

*Urinary calculi* are not unfrequent in some of the above and other animals. They vary considerably in composition. Carbonate of lime, carbonate of magnesia, phosphate of lime, and ammonio-magnesian phosphate, are common ingredients; they also often contain a considerable proportion of a peculiar animal matter, of a resinous or fatty character. Oxalate of lime has been detected by Fourcroy and Vauquelin, in the calculus of the *rat*; and in a calculus from a *dog*, Lassaigne found a substance which he terms *cystine* (p. 1838). Taylor found *urate of potassa* to be the leading ingredient in three calculi from the *iguana*. (*Phil. Mag.*, December, 1845.) In calculi from a *horse* I found phosphate and carbonate of lime, and ammonio-magnesian phosphate. Calculi from the *ox* sometimes abound in carbonate of lime. In a calculus from a *sheep* I found phosphate and carbonate of lime. The calculi of the *hog* sometimes consist chiefly of carbonate of lime, and sometimes of phosphate of lime, and ammonio-magnesian phosphate. In a large calculus from the bladder of a *dog* I also found phosphate of lime and ammonio-magnesian phosphate. (*Phil. Trans.*, 1808.)

## § VI. SOFT SOLIDS OF ANIMALS. SKIN. MUSCLE, &c.

THE skin of animals consists of an exterior covering, the *epidermis*, or *cuticle*, under which is a thin stratum of a peculiar substance, called by anatomists *rete mucosum*, which lies immediately upon the *cutis*, *corium*, *dermis*, or *true skin*.

The *epidermis* varies in thickness on different parts of the body; it is little prone to decomposition, insoluble in water, in alcohol, and in dilute acids. Concentrated nitric and sulphuric acid soften and ultimately dissolve it. The caustic fixed alkalis dissolve it, even when considerably diluted, but not the carbonated alkalis. It is stained by several substances, so far indelibly that the color remains till the cuticle peels off. It does not combine with tannine. Corns, and similar indurations, resemble the epidermis in their general chemical characters; and horn, hoof, nails, claws, tortoise-shell, hair, wool, feathers, and scales, may be regarded as modifications of it. All these substances partake more or less of the character of dry albumine, and Hatchett's researches have shown, that the analogies between them are in many cases only broken by the presence of foreign substances.

The general *color* of the surface of the body resides in the *rete mucosum*, the tint of which is much dependent upon the influence of light:



the black skin of the African, the brown of the Asiatic and American, and the pinkish-white of the European, derive their color from this peculiar secretion deposited between the *cutis* and *cuticle*; the nature of this substance has not been chemically investigated, but it has been ascertained in regard to the *black* of the negro, that it admits of being bleached by chlorine.

The *cutis*, or true skin, is of a fibrous texture, and when boiled in water is to a great extent soluble, leaving the vascular and nervous filaments which pervade it; the solution, when slowly evaporated, leaves *gelatine*, which is the principal and characteristic component of the *cutis*: the properties, composition, and sources of *gelatine* have been already described. (p. 1242.)

LEATHER is formed by steeping the skins of animals in the infusions of certain barks, or other *vegetable astringents*, and must be regarded as essentially consisting of a compound of tannine and *gelatine* (see p. 1246); many of its peculiarities are however referable to the texture and anatomical constitution of the skin, as well as to extractive, gallic acid, and other vegetable matters associated with the tannine in oak bark and other tanning materials, such as *valonia*, *sumach*, *catechu*, &c. There are also other organic and inorganic materials employed in the production of different kinds of leather.

In the manufacture of common *tanned leather*, the skins are previously prepared by soaking in lime-water, which renders the *cuticle* and hair easily separable, and are afterwards softened by allowing them to enter into a degree of putrefaction, or occasionally by the agency of acids. In this state they are submitted to the action of infusion of oak bark, or other astringent vegetable matter, the strength of which is gradually increased until a complete combination has taken place, which is known by the leather being of an uniform brown color throughout; whereas, in imperfectly tanned leather, a white streak is perceptible in the centre. Davy found the increase of weight in the skin, to vary with the tanning material; thus, 100 parts of calf skin, tanned in concentrated infusion of galls, increased in weight 64 parts; in a concentrated infusion of oak-bark, 34 parts; in a weak infusion, 17 parts; in concentrated infusion of willow bark, 34 parts, and in a weak infusion, 15 parts; and lastly, in a solution of *catechu*, 19 parts.

*Tawed leather* is made by impregnating the skin, duly prepared by washing in an alkaline liquor, with a solution of alum and common salt: it is afterwards trodden in a mixture of yolk of eggs and water. The alum and salt re-act on each other so as to produce sulphate of soda and chloride of aluminum; the latter salt combines with the skin. White glove leather is thus prepared.

*Wash leather* is another important manufacture; in this the skin, after having been prepared and softened, is imbued with oil, and afterwards subjected to a weak alkaline solution.

*Curried leather* is made by *bésmearing* the leather, while yet moist, with common oil, which, as the humidity evaporates, penetrates into the pores of the skin, giving it a peculiar suppleness, and making it, to a considerable extent, waterproof. As familiar examples of these processes, the thick sole leather for shoes and boots is *tanned*; the upper leather is

*tanned* and *curried*; the white leather for gloves is *tawed*; fine Turkey leather is *tawed*, and afterwards slightly *tanned*; and *buff*, like *wash leather*, is oil dressed. (AIKIN'S Dictionary, Art. LEATHER.)

MUSCLE. *Muscular flesh*, or *fibre*, consists chiefly of *fibrine* (p. 1227), mixed with cellular tissue, nerves, vessels, and fat; it also includes a large proportion of water, of which it may be deprived by careful desiccation at a low temperature *in vacuo*. When finely minced muscular fibre is digested in hot water, a quantity of soluble matter is taken up, consisting partly of *gelatine*, and partly of other substances, the insoluble residue being chiefly *fibrine*, with the vessels, &c. The relative proportions of these soluble and insoluble matters are not greatly different in the flesh of different animals, and may be averaged at 25 per cent. The following table shows the quantity of fibrine, and of gelatine, and soluble matters, thus afforded by the muscles of different animals, and representing, therefore, their relative nutritive values.

| 100 parts of<br>Muscle of | Water. | Fibrine, &c. | Gelatine, &c. | Total of<br>Nutritive Matter. |
|---------------------------|--------|--------------|---------------|-------------------------------|
| Beef .....                | 74     | 20           | 6             | 26                            |
| Veal .....                | 75     | 19           | 6             | 25                            |
| Mutton .....              | 71     | 22           | 7             | 29                            |
| Pork .....                | 76     | 19           | 5             | 24                            |
| Chicken .....             | 73     | 20           | 7             | 27                            |
| Cod .....                 | 79     | 14           | 7             | 21                            |
| Haddock .....             | 82     | 13           | 5             | 18                            |
| Sole .....                | 79     | 15           | 6             | 21                            |

The flesh of the ox (lean beef) has been examined by Berzelius, Braconnot, and Schlossberger, with the following results:

|  | Berzelius. | Braconnot. | Schlossberger. |
|--|------------|------------|----------------|
| Substances insoluble in cold water, fibrine, vessels, nerves, &c. .... | 17.70      | 18.18      | 17.5           |
| Soluble albumine, and coloring matter .....                            | 2.20       | 2.70       | 2.2            |
| Alcoholic extract and salts .....                                      | 1.80       | 1.94       | 1.5            |
| Aqueous extract and salts .....  | 1.15       | 1.15       | 1.3            |
| Phosphate of lime with albumine .....                                  | 0.08       |            |                |
| Water and loss .....   | 77.17      | 77.03      | 77.5           |
|  | 100.00     | 100.00     | 100.00         |

The following comparative analyses of different kinds of muscular flesh are by Schütz (*Vergleichende Chemische untersuchung von Fleisch*, 1841. LÖWIG. *Chem. d. Org. Verb.*, i. 557).

|                       | Beef.  | Veal.  | Young<br>pork. | 2 years old<br>pork. | Muscle of<br>Cyprinus<br>nasus. | Muscle of<br>Cyprinus<br>carpis. |
|-----------------------|--------|--------|----------------|----------------------|---------------------------------|----------------------------------|
| Water .....           | 77.50  | 75.70  | 70.98          | 72.18                | 80.00                           | 76.70                            |
| Albumine and cruor    | 4.30   | 2.34   | 3.45           | 4.20                 | 2.77                            | 2.35                             |
| Alcoholic extract     | 1.32   | 1.75   | 3.31           | 1.55                 | 1.38                            | 2.00                             |
| Aqueous extract ..... | 1.80   | 1.14   | 2.06           | 1.65                 | 2.15                            | 1.70                             |
| Fibrine .....         | 15.00  | 19.00  | 21.00          | 20.30                | 13.50                           | 17.18                            |
| Fat and loss .....    | 0.08   | 0.07   | 0.10           | 0.12                 | 0.09                            | 0.07                             |
|                       | 100.00 | 100.00 | 100.00         | 100.00               | 100.00                          | 100.00                           |

According to Schütz, pork always contains more fibrine than veal or



beef; the flesh of young animals abounds in alcoholic extract, and that of older animals, in aqueous extract; the former also abounds in salts of soda, the latter in salts of potassa: he also observes that the fibrine of young animals is more soluble in acids, and therefore easier of digestion, than that of older animals. The recent researches of Liebig, to which I shall presently refer, have, however, thrown further light upon this subject.

It appears from the analyses of Playfair and Böckmann (quoted by Liebig), that the *ultimate constituents* of dry muscle (*beef* deprived of fat) are the same as those of dried blood, namely,

|                  | Dry muscle. |       | Dry blood. |
|------------------|-------------|-------|------------|
| Carbon.....      | 51.893      | ..... | 51.965     |
| Hydrogen .....   | 7.590       | ..... | 7.330      |
| Oxygen, &c. .... | 19.127      | ..... | 19.115     |
| Nitrogen .....   | 17.160      | ..... | 17.175     |
| Ashes .....      | 4.230       | ..... | 4.415      |
|                  | <hr/>       |       | <hr/>      |
|                  | 100.000     |       | 100.000    |

According to the analysis of Enderlin, the *ashes* from 1000 parts of *beef*, are constituted as follows:

|   |        |            |
|---|--------|------------|
| Tribasic phosphate of soda .....          | 45.100 | } = 97.876 |
| Chlorides of potassium and of sodium .... | 45.936 |            |
| Phosphates of lime, magnesia, and iron    | 6.840  |            |

Under the term *alcoholic extract*, in the preceding analyses, a substance is included which Thenard termed *osmazome* (from *οσμη*, odor, and *ζωμος*, broth), and which he obtained by evaporating the watery extract of flesh to dryness, and digesting the residue in alcohol: the evaporation of this alcoholic solution left the *osmazome* in the form of a transparent brown extract, of a strong odor and flavor, resembling that of dressed meat; it was further distinguished by solubility in water and alcohol, and by yielding a precipitate with infusion of galls, but not gelatinizing. But recent experiments have shown that *osmazome* is a mixture of several substances; so also *zomidine*, a product of the aqueous extract of flesh, contains other proximate principles. One of the most remarkable of these substances, extracted from muscular fibre, was discovered by Chevreul (*Journ. de Pharm.*, xxi. 236), and termed *kreatine*; its sources and properties have lately been investigated by Liebig and by Gregory. (*Researches on the Chemistry of Food*, London, 1847. *Turner's Elements of Chemistry*, 8th edit., p. 1280.)

These chemists observe, that besides the blood, and the fluids contained in the absorbents and lymphatics of muscles, there exists in them a peculiar fluid, enclosed either in peculiar vessels, or in the cellular tissue, which they distinguish under the name of *juice of flesh*, and which is remarkably characterized by its inherent *acidity*, while the blood is always alkaline: they have also inquired into the cause of this acidity, and have minutely examined the other soluble constituents of muscular flesh.

Liebig gives the following directions in reference to these investigations. About 10 lbs. of the flesh of the recently killed animal, after having been freed as far as possible from blood, fat, vessels, tendons, &c., is finely minced, and then well kneaded with about its weight of cold

distilled water; the whole is then strained through a piece of coarse linen, and the residue well pressed out; this residue is then similarly treated a second, and, if requisite, a third time, so as to extract all its soluble matters, which amount upon the average to not more than from 4 to 6 *per cent.* of the original flesh. The liquor thus obtained is turbid, of a more or less reddish tint, its color depending upon its source; it has the taste and smell of meat, and is always *acid*, a property, which, as Liebig observes, is the more worthy of notice, inasmuch as it always contains *blood*, which is *alkaline*, and yet insufficient to neutralize the *acid* of the flesh. "Indeed, I believe," he says, "that in most animals, if we suppose the whole mass of blood in the vessels to be mixed with the whole of the fluid in the muscles, the mixture would retain, not a neutral, or alkaline, but an acid reaction: in the hare, the amount of whose blood is proportionally small, this is certainly the case."

This acid liquor is then put into a glass flask immersed in a water-bath, and gradually heated up to about  $140^{\circ}$ , when the albumine which it contains, coagulates, and separates in nearly white flakes; when the temperature rises to  $158^{\circ}$ , the coloring matter of the blood (some of which is always present) also separates in the form of a brown coagulum; the heat is then continued till a filtered portion of the liquor, when *boiled in a test-tube*, remains clear. The whole is then strained, and an acid liquor is obtained, nearly colorless, and free from albumine; it contains all the soluble ingredients of the flesh not coagulable by heat, amongst which are kreatine and kreatinine, phosphoric acid, lactic acid, inosinic acid, and salts of potassium and sodium, and of magnesia and lime.

KREATINE.  $C_8H_9O_4N_3 + 2H_2O$ . If this acid liquor be evaporated, its free acid, and the other substances present, react upon each other, and a brown extract is obtained. To prevent this, Liebig and Gregory proceed as follows: the free acid is neutralized by adding baryta-water, as long as it occasions a precipitate; the liquor becomes distinctly alkaline before this point is reached, but when turmeric paper is rendered distinctly brown, a sufficiency of baryta has been added. The white precipitate is phosphate of baryta, and contains the whole of the phosphoric acid in the juice. A mere trace of sulphate of baryta, derived probably from the presence of little blood in the juice, is sometimes found in it. This phosphate is separated by filtration, and the filtered liquor, now very slightly alkaline, is evaporated in shallow dishes, in a water-bath, at a temperature not exceeding  $140^{\circ}$ ; a little insoluble matter separates, and when the whole is considerably reduced in bulk, it is again filtered, and the clear liquor evaporated at  $130^{\circ}$  to the consistence of thin syrup. Any films which separate during this evaporation must be carefully removed; the concentrated liquor is then allowed to stand for a day or two, at a temperature between  $80^{\circ}$  and  $90^{\circ}$ , and then set aside in a cold place, when crystals of kreatine gradually form in it, which are purified by solution in 6 or 7 parts of boiling water, from which they recrystallize in the form of brilliant colorless prisms. Gregory observes that it often happens that, after the last filtration, and towards the end of the evaporation, a brown powder separates, and mixes with the crystals, and which is chiefly composed of kreatine; in one case, in which he used ox-heart, he obtained no crystals, but only this powder, which however was dissolved



almost entirely by boiling water, and yielded rather more kreatine in proportion to the flesh employed, than was obtained in another similar experiment in which the kreatine crystallized as usual. In endeavoring to obtain kreatine from pike, Liebig found some difficulty, in consequence of the gelatinous character of the flesh ; but Gregory states that he found no such difficulty with skate and cod, which were very easily pressed and extracted; he evaporated the liquor till it formed a very thin jelly on cooling; he let this stand for two days, and then added a sufficient quantity of cold water to liquefy it, after which it deposited crystals of kreatine, very pure and colorless. The amount of kreatine obtainable from the different kinds of flesh hitherto examined, varies from 0·6 to 3·2 *per* 1000. Thus,

|   |              |
|---|--------------|
| 1000 parts of flesh of fowl yielded ..... | 2·90 to 3·20 |
| „ ox heart .....                          | 1·37 to 1·41 |
| „ cod .....                               | 0·93 to 1·71 |
| „ pigeon .....                            | 0·82         |
| „ horse .....                             | 0·72         |
| „ ox .....                                | 0·69         |
| „ skate .....                             | 0·60         |

Gregory observes, that, although fowl contains more kreatine than any other flesh yet tried, the most economical source of it is skate or cod; that with it the whole operation is easier, and the kreatine obtained nearly pure, from the gelatinizing liquid: when only once recrystallized, and without the use of any decolorising agent, it was snow-white, and chemically pure. From 25 pounds of cleaned cod he obtained 164 grains of kreatine ; and in another experiment, from 30 lbs., the large amount of 356 grains.

*Kreatine* forms either brilliant acicular prisms, or short thick transparent crystals, of adamantine lustre: the latter are deposited from the less concentrated solutions: heated to 212°, they become opaque, and lose about 12 *per cent.* of water. It dissolves in between 6 and 7 parts of water at 212°, but the greater part is deposited on cooling: the cold water then only retains about 1-30th of its weight in solution, and if the crystals be left in it, they increase in size; so that 1 part of kreatine, requires for its permanent solution, about 75 of cold water. The solution has a slightly bitter taste. Kreatine is very sparingly soluble in alcohol. It has neither acid nor basic properties. The elements of crystallized kreatine are,

|                              |    |     |     |     |        |     |                  |       |                         |   |     |     |     |        |
|------------------------------|----|-----|-----|-----|--------|-----|------------------|-------|-------------------------|---|-----|-----|-----|--------|
| Carbon .....                 | 8  | ... | 48  | ... | 32·22  | ... | Liebig.<br>32·41 | } = { | Anhydrous }<br>kreatine | 1 | ... | 131 | ... | 87·92  |
| Hydrogen ....                | 11 | ... | 11  | ... | 7·38   | ... | 7·39             |       |                         |   |     |     |     |        |
| Oxygen .....                 | 6  | ... | 48  | ... | 32·22  | ... | 31·88            |       |                         |   |     |     |     |        |
| Nitrogen ....                | 3  | ... | 42  | ... | 28·18  | ... | 28·32            |       |                         |   |     |     |     |        |
| <hr/>                        |    |     |     |     |        |     |                  |       |                         |   |     |     |     |        |
| Crystallized }<br>kreatine } | 1  |     | 149 |     | 100·00 |     | 100·00           |       |                         |   |     |     |     |        |
| <hr/>                        |    |     |     |     |        |     |                  |       |                         |   |     |     |     |        |
|                              |    |     |     |     |        |     |                  |       |                         | 1 |     | 149 |     | 100·00 |

KREATININE. C<sub>8</sub> H<sub>7</sub> O<sub>2</sub> N<sub>3</sub>. When a solution of kreatine in hydrochloric acid is evaporated to dryness, the substance which remains is a *hydrochlorate of kreatinine*. So also when kreatine is mixed with dilute sulphuric acid, in the proportion of 1 part of kreatine, and 1 of acid composed of 27 parts of oil of vitriol and 73 parts of water, and evaporated

to dryness, and heated till all moisture is expelled, a neutral *sulphate of kreatinine* is the result. It appears therefore, that under the influence of the stronger acids, kreatine, which is a neutral or indifferent body, becomes converted into kreatinine, which is powerfully basic, and that this conversion is effected by the abstraction of the elements of 4 atoms of water. To isolate the kreatinine, the *hydrochlorate* is dissolved in from 24 to 30 parts of water, the solution heated to its boiling-point in a porcelain basin, and hydrated oxide of lead, suspended in water, added in small quantities at a time. At first, chloride of lead is formed, and the liquor retains its acid reaction; but on the further addition of the oxide, it becomes neutral, and then slightly alkaline. If now there be added to the mixture a quantity of oxide of lead three times as great as that already employed, and the whole kept boiling for some time, a point is at last reached at which the liquid, no matter how much diluted, seems to be converted into a yellow pasty mass: the decomposition is then complete; the liquid is filtered, and the residue carefully washed. Should a trace of oxide of lead be dissolved, or suspended in the filtered liquid, it is easily removed by means of a little animal charcoal. This process depends upon the conversion of the chloride of lead, into a basic compound with oxide of lead, (oxichloride of lead), which is as insoluble in water as chloride of silver. The solution thus obtained, is free from chlorine, and yields, on evaporation, crystals of kreatinine. Kreatinine may also be obtained by decomposing its *sulphate*, by the addition of carbonate of baryta to its boiling solution, till no further effervescence ensues, and the liquid has an alkaline reaction; it is then filtered, and yields kreatinine on evaporation. (LIEBIG.)

*Kreatinine* forms prismatic crystals, soluble in between 11 and 12 parts of water at  $60^{\circ}$ , and in about 100 parts of alcohol at the same temperature. It has an alkaline reaction upon reddened litmus, and upon turmeric paper, and in its chemical relations it has some analogy to ammonia; it expels ammonia from ammoniacal salts; with the salts of oxide of copper, it forms crystallizable double salts, of a fine blue color. When added to a solution of nitrate of silver, it forms a basic compound with that salt, which crystallizes in small white needles. In a solution of corrosive sublimate it causes a white curdy precipitate, which soon changes to a mass of slender acicular crystals. In a neutral aqueous solution of chloride of zinc it causes a granular precipitate, appearing under the microscope to be made up of concentric groups of small needles. When hydrochlorate of kreatinine is added to dilute bichloride of platinum, there is no precipitate; but on evaporation, deep yellow crystals of a double salt are obtained.

In 1844 Pettenkofer discovered a substance in urine, characterized by forming a crystalline compound with chloride of zinc. (*Ann. der Pharm.*, lii. 97.) Liebig has ascertained that this property is derived from the presence of kreatine and kreatinine in that excretion; to obtain them, he neutralizes the urine by lime, and then adds chloride of calcium, so as to precipitate the phosphoric acid: the liquor is then filtered, evaporated to the consistence of thin syrup, and set aside to crystallize. The mother-liquor is then poured off, and to every pound of it, about half an ounce of a saturated solution of chloride of zinc is added. On standing for a few days, the mixture deposits a crystalline compound, consisting of



kreatine, mixed with the above-mentioned combination of kreatinine with chloride of zinc; this mixture is washed with a little cold water, then dissolved in boiling water, and boiled for half an hour with excess of hydrated oxide of lead; the filtrate is next boiled with a little blood-charcoal, evaporated to dryness in a water-bath, and the residue boiled in 8 or 10 parts of alcohol; on cooling, kreatine is deposited, and kreatinine remains in the mother-liquor.

The elements of kreatinine are

|                  |   |      |     |      |        | Liebig.    |
|------------------|---|------|-----|------|--------|------------|
| Carbon .....     | 8 | .... | 48  | .... | 42.48  | .... 42.54 |
| Hydrogen .....   | 7 | .... | 7   | .... | 6.19   | .... 6.38  |
| Oxygen .....     | 2 | .... | 16  | .... | 14.16  | .... 13.88 |
| Nitrogen.....    | 3 | .... | 42  | .... | 37.17  | .... 37.20 |
| <hr/>            |   |      |     |      |        |            |
| Kreatinine ..... | 1 |      | 113 |      | 100.00 | 100.00     |

*Hydrochlorate of Kreatinine.*  $C_8H_8O_2N_3Cl = C_8H_7O_2N_3 + HCl$ . This salt readily dissolves in boiling alcohol, and crystallizes from it in short transparent colorless prisms, very soluble in water, and deposited from its aqueous solution, in broad transparent scales, having an acid reaction. A saturated solution of this salt in boiling alcohol, neutralized by ammonia, yields transparent granular crystals of kreatinine, on cooling.

*Sulphate of Kreatinine*,  $C_8H_7O_2N_3, HO, SO_3$ , crystallizes from its hot alcoholic solution, in transparent 4-sided tables.

**SARCOSINE.**  $C_6H_7O_4N$ . This is a basic compound, discovered by Liebig, and obtained by boiling kreatine with 10 times its weight of crystallized hydrate of baryta: the solution remains at first clear, but afterwards evolves ammonia, and deposits a white crystalline powder: if boiled till no further escape of ammonia is perceptible, the filtered liquor contains baryta combined with sarcosine, and carbonate of baryta remains upon the filter. On passing carbonic acid through the filtrate, carbonate of baryta is deposited, and sarcosine remains dissolved, and may be obtained by evaporating the solution to the consistence of syrup, when it concretes, on cooling, into a mass of broad colorless transparent plates. This first product may be purified by digesting it in dilute sulphuric acid, evaporating the sulphate in a water-bath, adding alcohol to the syrupy residue, and stirring the mixture, when it deposits the *sulphate of sarcosine*, in the form of a white crystalline powder. This, decomposed by pure carbonate of baryta, yields a solution of pure sarcosine, from which crystals may be obtained by evaporation.

*Sarcosine* crystallizes in right rhombic prisms, colorless, and transparent; they are very soluble in water, sparingly soluble in alcohol, and insoluble in ether. Dried at  $212^\circ$ , they retain their original aspect, and at a somewhat higher temperature, melt, and sublime without residue. The aqueous solution of sarcosine has no action on vegetable colors; it has a sweetish, sharp, and somewhat metallic taste; it causes no change in dilute solutions of nitrate of silver, or of corrosive sublimate; but if a crystal of sarcosine be placed in a cold saturated solution of corrosive sublimate, it is immediately dissolved, and transparent needles of a double salt are soon copiously deposited. A solution of acetate of copper acquires from sarcosine the same deep blue color as from ammonia. A solution

of *hydrochlorate of sarcosine*, mixed with excess of bichloride of platinum, gives no precipitate, but by spontaneous evaporation, deposits yellow octohedral crystals. Sarcosine is composed of

|                 |   |     |    |     |        |     |                  |
|-----------------|---|-----|----|-----|--------|-----|------------------|
| Carbon .....    | 6 | ... | 36 | ... | 40.45  | ... | Liebig.<br>40.73 |
| Hydrogen .....  | 7 | ... | 7  | ... | 7.86   | ... | 7.90             |
| Oxygen .....    | 4 | ... | 32 | ... | 35.96  | ... | 35.53            |
| Nitrogen .....  | 1 | ... | 14 | ... | 15.73  | ... | 15.84            |
| <hr/>           |   |     |    |     |        |     |                  |
| Sarcosine ..... | 1 |     | 89 |     | 100.00 |     | 100.00           |

Liebig observes that the composition of sarcosine explains its production from kreatine: if from an atom of crystallized kreatine =  $C_8H_{11}O_6N_3$ , we deduct an atom of sarcosine, =  $C_6H_7O_4N$ , there remains  $C_2H_4O_2N_2$ , which is *urea*; and he has shown, that in this process urea is actually separated, but that by the action of the baryta and water at its boiling point, it is resolved into carbonic acid and ammonia. Liebig further observes, that sarcosine is isomeric with *lactamide* (p. 1792) and with *urethane* (p. 1695), but that it is distinguished from those compounds, by its basic characters, and by its sparing solubility in alcohol, and insolubility in ether.

**INOSINIC ACID.**  $C_{10}H_6O_{10}N_2 + HO$ . When the syrupy liquid which has deposited the crystals of kreatine, is further concentrated by evaporation, and mixed with alcohol till it becomes milky, a deposit is formed, which dissolved in warm water, and mixed with chloride of barium, gives a precipitate consisting chiefly of *inosinate of baryta*; it may be purified by recrystallization from warm water, but if boiled, it is decomposed. By decomposing *inosinate of baryta* by sulphuric acid, or *inosinate of copper* by sulphuretted hydrogen, the inosinic acid is separated.

*Inosinic acid* has a strong acid reaction, and possesses an agreeable taste of the juice of meat. When evaporated to the consistence of syrup, it does not crystallize, but on the addition of alcohol, forms a white pulverulent mass. It is insoluble in ether. It does not precipitate lime or baryta water. The free acid, and its soluble salts, added to a solution of acetate of copper, throw down *inosinate of copper*, in the form of an insoluble greenish-blue precipitate; with nitrate of silver, they give a white gelatinous precipitate, soluble in nitric acid, and in ammonia; with the salts of lead the precipitate is also white. Liebig observes that the temperature at which the solution of the juice of flesh is evaporated, materially influences the preparation of inosinic acid; and that it appears to be occasionally absent, and not to occur in fish. It exists in flesh, as *inosinate of potassa*. The components of the anhydrous acid, as it exists combined with baryta, are, according to Liebig,

|                              |    |     |     |     |        |
|------------------------------|----|-----|-----|-----|--------|
| Carbon .....                 | 10 | ... | 60  | ... | 34.46  |
| Hydrogen.....                | 6  | ... | 6   | ... | 3.45   |
| Oxygen.....                  | 10 | ... | 80  | ... | 45.97  |
| Nitrogen .....               | 2  | ... | 28  | ... | 16.10  |
| <hr/>                        |    |     |     |     |        |
| Anhydrous inosinic acid .... | 1  |     | 174 |     | 100.00 |

*Inorganic Constituents of the Juice of Flesh.* Liebig ascribes the acid



reaction of the juice of flesh, to the presence of acid salts of the alkalis with phosphoric, lactic, and inosinic acids; and principally to acid lactates and acid phosphates. Of the latter, the principal is *phosphate of potassa*, a salt remarkable for its tendency to assume the acid modification  $=\text{KO}, 2\text{HO}, \text{PO}_5$ ; whereas *phosphate of soda*, the principal salt of the blood, tends to the alkaline modification  $=2\text{NaO}, \text{HO}, \text{PO}_5$ . The ash of the juice of flesh is almost entirely soluble in water, and contains no carbonate; it consists chiefly of alkaline phosphates and chlorides, of which potassium is the predominant basis; whereas in the blood, the salts of sodium prevail.

The following practical applications, deduced from the preceding statement respecting the composition of muscular flesh, are principally abridged from Liebig's *Researches*, (§ iii., p. 122.) He observes, that in the common culinary process of boiling meat, the water will abstract the soluble alkaline phosphates, lactates, and inosinates, with a little phosphate of magnesia, and traces of phosphate of lime; and that the insoluble inorganic constituents, chiefly phosphate of lime and phosphate of magnesia, will be retained in combination with the fibrine, albumine, &c., in the boiled flesh: and further, that if flesh employed as food, is again to become flesh in the body, none of the constituents of the raw flesh ought either to be withdrawn or materially changed; so that boiled meat, when eaten without the soup or liquor in which it is boiled, (the *bouilli* without the *bouillon*), is less adapted for nutrition, in proportion to the quantity of water in which it has been boiled, and the duration of the boiling.

When minced meat is triturated with cold water, it loses its soluble constituents, amongst which is *albumine*, and the fibrinous residue, if boiled, is found to be very insipid; showing that the taste and odor of the meat depend upon the soluble constituents which are contained in the broth.

These soluble constituents are also the source of the flavor of *roasted meat*, in which, however, they are modified by the higher temperature. Flesh therefore, which has been rendered tasteless by boiling in water, acquires the flavor and peculiarities of roasted meat, when moistened with a cold aqueous infusion of raw flesh evaporated till it has acquired a dark brown color. What is known in the kitchen under the name of *stock*, is in fact, as Dr. Gregory has observed, this concentrated infusion of flesh: it is used to impart and improve flavor, and to restore the soluble matters removed in previous operations. The advantage of *stewing* over boiling, and the folly of boiling meat in a large quantity of water which is afterwards thrown away, are also now sufficiently obvious.

It is stated by Liebig, that the quantity of albumine abstracted by cold water from different kinds of flesh is not only different in different animals, but also varies with their age, and is most abundant in young animals; he says, that the flesh of the horse yields not more than a tenth part of the quantity of albumine furnished by the same weight of beef; and further, that the residuary fibrine of the flesh is of the same quality in all animals. He refers the *tenderness* of dressed meat to the coagulated albumine deposited between the fibres, by which their induration is to a certain extent prevented; and directs, as the most scientific mode of boiling meat, that it should be put into the water in a state of brisk

ebullition, which should be kept up for some minutes, and then, so much cold water added, as to reduce the temperature to about  $160^{\circ}$ , and the whole kept at that temperature for some hours. By this mode of treatment, the albumine coagulates from the surface inwards, and prevents the penetration of the water into the interior of the mass, the temperature of which is, however, raised to the due point for the production of sapid matter, and all the juiciness retained. As albumine is completely coagulated at  $140^{\circ}$ , it might be supposed that that temperature would be adequate; but the *coloring matter of the blood* requires a higher temperature for its coagulation; and we accordingly observe, that although meat dressed at a temperature of about  $140^{\circ}$  is eatable, it has a disagreeable bloody appearance, which it loses at  $160^{\circ}$ . So that by the successive colors of the interior of a large piece of dressed meat, we can tell the temperatures to which its different parts have attained, and which have always been below  $144^{\circ}$  when they are red or bloody. “In the boiling or roasting of poultry, the flesh of which is white, and contains little blood, the temperature of the inner parts, when the flesh has been well cooked, seldom exceeds  $130^{\circ}$  or  $140^{\circ}$ : the flesh therefore of poultry or game is sooner dressed (*ready*, or *done*, as it is called) than flesh which contains much blood, such as beef or mutton.”

By attention to these rules, the perfection of the dressed joint is ensured; but, where the object is to obtain good *soup*, other methods must be adopted; the flesh must be cut into thin slices and put into cold water, which must be raised, *very gradually*, to the boiling-point; the water in this way penetrates the flesh and dissolves its sapid constituents; the albumine is abstracted, and as it coagulates, it rises to the surface and may be skimmed off, whilst the residuary fibre, losing its tenderness and *shortness*, becomes hard and insipid, and less digestible and nutritious, inasmuch as the very substances which are contained in the soup, namely the acids and salts of the flesh, are constituents of the gastric juice.

The peculiarities of good soup, that is, its flavor and its nutritive powers, have often been ascribed to *gelatine*, a portion of which is of course always contained in it, and gives it the property of gelatinizing when cold; but, in the first place, gelatine is, in all states, an insipid substance; and in the next, the absolute amount of pure gelatine contained in meat, is very small, and of that, only a small part is extracted in the usual process of boiling. According to Liebig, we obtain from 1000 parts of beef,

|  |         |                                |     |
|--|---------|--------------------------------|-----|
|  |         | By boiling.                    |     |
| Substances soluble in cold water       | .... 60 | { Coagulated albumen.....      | 30  |
|  |         | { Retained in solution .....   | 30  |
| Substances insoluble in cold water.... | 170     | { Gelatine in solution .....   | 6   |
|  |         | { Fibre, &c. (insoluble) ..... | 164 |
| Fat .....                              | 20      |                                |     |
| Water .....                            | 750     |                                |     |
|  | <hr/>   |                                |     |
|  | 1000.   |                                |     |

So that the efficacy of soup or broth cannot be referred to the gelatine which it holds in solution.

It will now be obvious that the most economical mode of making broth or soup, consists in mincing the meat, and subjecting it to the action of cold water, very gradually raised to its boiling-point. “When 1 pound of lean beef, free from fat and bone, in the finely-chopped state in



which it is used for beef sausages or mince-meat, is uniformly mixed with its own weight of cold water, slowly heated to boiling, and the liquid, after boiling briskly for a minute or two is strained through a cloth from the coagulated albumine, and from the fibrine now become hard and horny, we obtain an equal weight of the most aromatic soup, of such strength as cannot be obtained, even by boiling for hours, from a piece of flesh. When mixed with salt, and other usual additions by which soup is seasoned, and tinged with roasted onions, or burned sugar, it forms the very best soup which can in any way be prepared from a pound of meat."

In consequence of the ideas of strength and concentration, associated with *color*, its addition gives an imaginary flavor to the soup, so that it is supposed to be stronger when the burnt sugar is added. The real quantity of true *extract of flesh* obtained from 32 pounds of lean beef, (that is, from 8 pounds of *dry meat*, and 24 of water,) amounts, according to Liebig, to not more than 1 pound; and this constitutes *genuine portable soup*; its high price, however, would alone prevent its general use. The tablets usually called "portable soup" are merely bone gelatine, and a very inadequate and deceptive substitute therefore for meat.

In the process of *salting meat*, the liquor, or *brine*, which runs off, contains the chief constituents of concentrated soup, including a large proportion of albumine; it has an acid reaction, and contains ammonio-magnesian phosphate, lactic acid, potassa, and kreatine; in the *process of salting*, therefore, a number of important principles are abstracted from the flesh, which, if not afterwards supplied in other forms, leave it in an unfit condition for food. The production of scorbutic affections, and the influence of certain organic acids in their cure, seem to be, to a certain extent explained by reference to these facts.

## § VII. SHELL, CORAL, AND BONE.

WE are indebted to Hatchett for two dissertations on the chemical properties of these parts of animals, published in the *Philosophical Transactions* for 1799 and 1800. He has divided *shells* into two classes; the texture of the first is compact, brittle, and resembling porcelain; their surface is smooth, and they are often beautifully variegated. When exposed to a red heat they crackle, and lose the color of their enamelled surface, emitting scarcely any smoke or smell. They dissolve in dilute hydrochloric acid with copious effervescence, and form a transparent solution, in which, neither pure ammonia, nor acetate of lead, produces any precipitate; but carbonate of ammonia throws down carbonate of lime. Hence these, which are called *porcellaneous shells*, may be considered as chiefly composed of carbonate of lime, united to a very small portion of gelatine: most of the univalve shells, such as whelks, limpets, cowries, and many of the beautiful convoluted shells of tropical countries, belong to this class.

The second class, or *mother-of-pearl shells*, are tougher, glossy, and iridescent: they are mostly bivalves, and all the oyster and muscle species belong to it. When heated, they exhale smoke, and the smell of burned horn; immersed in hydrochloric acid, they only partially dissolve, and leave a series of cartilaginous layers, and an outer epidermis. Each membrane appears to have a corresponding stratum of carbonate of lime,

the solution indicating no trace of any phosphate. The animal part is in some cases, as in mother-of-pearl, tough and indurated; and when dried, becomes like horn; in other instances, as in the bone of the cuttle fish, it appears in the form of delicate and tender membranes.

In both classes of shells, therefore, the hardening principle is carbonate of lime; in porcellaneous shells there is very little animal matter, which is gelatine; but in mother-of-pearl shells, it is cartilaginous, and in larger quantities.

*Pearls* are exactly similar in composition to what is termed *mother-of-pearl*, in which Hatchett found carbonate of lime 66, animal matter 54.

*Corals* or *Zoophytes*, according to Hatchett's researches, may be divided into four classes: 1. The first class resembles porcellaneous shells, and consists entirely of carbonate of lime, with a very minute quantity of animal matter; of this, the common white coral (*Madrepora virginea*) is an example. 2. The second consists of carbonate of lime, and a cartilaginous substance, and is therefore analogous to mother-of-pearl shell, to this class belong the *Madrepora ramea*, and *Madrepora fascicularis*. 3. The third class is composed of a cartilaginous matter, with carbonate and phosphate of lime; to this belongs the red coral. (*Gorgonia nobilis*.) 4. The fourth class contains sponges, composed almost entirely of animal matter. (*Phil. Trans.*, 1800.)

Some curious facts respecting the structure of sponge were communicated by Mr. Bowerbank to the *Microscopical Society* in 1841, and to the Royal Society in 1842. (*Phil. Trans.*, p. 215.)

*Sponge* has also been examined by Posselt (*Ann. der Pharm.*, xlv. 192) and by Croockewit (*ibid.* xlviii. 43). According to their analyses, after it has been exhausted by alcohol, ether, dilute hydrochloric acid, and water, it consists of

|                 | Croockewit.  |       | Posselt.     |
|-----------------|--------------|-------|--------------|
| Carbon .....    | 47.16        | ..... | 48.74        |
| Hydrogen .....  | 6.32         | ..... | 6.27         |
| Oxygen .....    | 26.90        | ..... | 28.59        |
| Nitrogen .....  | 16.15        | ..... | 16.40        |
| Sulphur .....   | 0.49         |       |              |
| Phosphorus..... | 1.90         |       |              |
| Iodine .....    | 1.03         |       |              |
|                 | <hr/> 100.00 |       | <hr/> 100.00 |

*Bone*, and *Ivory*, like the preceding substances, are essentially composed of soft and hard parts. When ground bone is digested in warm water, a portion of fat is first separated, and by long-continued ebullition, a solution, which gelatinizes on cooling, is obtained. If fresh bone be immersed in diluted hydrochloric acid, the bony matter is dissolved, and a kind of skeleton of the bone remains, in the form of a cartilaginous substance, which, when dried, exactly resembles horn. It appears, therefore, that the soft parts of bone are, *fat*, *gelatine*, and *albumine*. The solution of bone-gelatine is distinguished from that of isinglass, by the copious precipitate which the former yields with oxalate of ammonia.

The earthy salts, which constitute the hard part of bone, are phosphate and carbonate of lime, with a minute quantity of sulphate of lime, and traces of phosphate of magnesia. Fourcroy and Vauquelin obtained from *ox bones*, animal matter 51.0, phosphate of lime 37.7,





A variety of *diseased bones* have also been analysed by Nasse. (*Chem. Gaz.*, July, 1843.)

The *enamel of teeth* is perfectly destitute of cartilage, and consists chiefly of phosphate of lime and a portion of gelatine. Pepys found its component parts, phosphate of lime 78, carbonate of lime 6, gelatine 16.

The same chemist has given the following as the composition of the substance of the teeth. (Fox, *On the Teeth*.)

|                         | Roots of<br>the Teeth. | Teeth of<br>Adults. | First Teeth<br>of Children. |
|-------------------------|------------------------|---------------------|-----------------------------|
| Phosphate of lime ..... | 58                     | 64                  | 62                          |
| Carbonate of lime ..... | 4                      | 6                   | 6                           |
| Cartilage .....         | 28                     | 20                  | 20                          |
| Water and loss.....     | 10                     | 10                  | 12                          |
|                         | <hr/> 100              | <hr/> 100           | <hr/> 100                   |

The difference between the structure and composition of the enamel and bone of teeth, is well illustrated in the teeth of some of those graminivorous animals, in which the enamel, instead of being external, alternates in layers with the bone: the section, for instance, of the elephant's tooth exhibits three distinct substances, namely, a hard and a softer bone, and an enamel; when steeped in dilute hydrochloric acid, the latter is entirely dissolved; but the bony portions leave variable proportions of cartilage.

We have as yet but few accurate comparative analyses of the bones of different animals. In human bone carbonate of lime is much more abundant, according to Berzelius, than in that of the ox: the relative proportions of these salts also vary considerably in other cases, as is shown in the following analyses of the earthy residue of different bones, by De Barros. (*Berzelius' Lehrbuch*.)

|             | Phosphate of Lime. | Carbonate of Lime. |
|-------------|--------------------|--------------------|
| Lion .....  | 95·0               | 2·5                |
| Sheep ..... | 80·0               | 19·3               |
| Hen.....    | 88·9               | 10·4               |
| Frog .....  | 95·2               | 2·4                |
| Fish.....   | 91·9               | 5·3                |

The bones of the pig have been examined in reference to their earthy constituents at different periods of the growth of the animal, by Bous-singault. (*Ann. Ch. et Ph.*, 3ème Sér., xvi. 486.)

The *bones of fish* contain less earthy matter than those of quadrupeds or birds. According to Chevreul, the bones of the head of the *cod* contain, animal matter and moisture 43·94, phosphate of lime 47·96, carbonate of lime 5·50, phosphate of magnesia 2·00, soda-salts, chiefly chloride, 0·60. The bones of the *haddock* contain, according to Dumenil, animal matter 37·63, phosphate of lime 55·26, carbonate of lime 6·16, traces of soda, salts, and loss, 1·22.

Marchand analysed a vertebra of the *Squalus Cornubicus*, from which he obtained 58·07 *per cent.* animal matter, 32·46 phosphate of lime, 4·44 carbonate and sulphate of lime, 1·03 phosphate of magnesia, 3·8 of soluble soda-salts, and 1·20 of fluoride of calcium, silica, and alumina. From a bone of the head of the *Squalus peregrinus*, he obtained 78·46 of animal matter, 14·20 phosphate of lime, 3·44 carbonate and sulphate of lime, 3·16 soluble soda-salts, and 0·74 fluoride of calcium, &c. (*Lehrbuch der Physiologischen Chemie*, Berlin, 1842.)



*Fossil Bones.* The following have been analysed by Marchand.  
 1. Bone of a bear found near the surface of the soil in the Gailenreuth cavern. 2. A similar bone from a considerable depth. 3. Upper thigh-bone of a fossil stag.

|                                | I.    |      | II.   |      | III.  |
|--------------------------------|-------|------|-------|------|-------|
| Animal substances.....         | 4·20  | .... | 16·24 | .... | 7·25  |
| Phosphate of lime .....        | 62·11 | .... | 56·01 | .... | 54·15 |
| Carbonate of lime .....        | 13·24 | .... | 13·12 | .... | 19·26 |
| Sulphate of lime.....          | 12·25 | .... | 7·14  | .... | 12·24 |
| Fluoride of calcium .....      | 2·12  | .... | 1·96  | .... | 2·08  |
| Phosphate of magnesia .....    | 0·50  | .... | 0·30  | .... | 2·12  |
| Silica .....                   | 2·12  | .... | 2·15  | .... |       |
| Oxide of iron, manganese, &c.. | 3·46  | .... | 3·08  | .... | 2·90  |

Several analyses of fossil bones have also been made by Girardin and Preisser. (*Ann. Ch. et Ph.*, November, 1843.) In some of them, the *bone phosphate* appears to have been resolved into other subphosphates of lime, and among them were found small crystals of apatite. The authors suppose that the bone phosphate =  $8\text{CaO}, 3\text{PO}_5$ , had become  $2\text{CaO}, \text{PO}_5$ , and  $2(3\text{CaO} \text{PO}_5)$ . Dr. Daubeny also found fluoride of calcium in various specimens of fossil bone, and succeeded in detecting it in recent human bone, and in the recent tooth of an ox, (*Mem. Ch. Soc.*, ii. 97.) It has also been found in recent bone by Mr. Middleton (*ibid.* p. 134), who is of opinion that traces of fluorine are to be found in ordinary water, and that it may therefore be contained in almost all vegetables, and be transferred from them into the animal system. Dr. Daubeny, however, could find no traces of fluorine in the phosphates derived from 12 pounds of barley.

The cartilaginous part of the bone is that which is first formed, as seen in the skeletons of young animals; and in the case of a bone being broken, the animal portion is first secreted, and it is gradually hardened by the deposition of the earthy salts, so as perfectly to reunite the fractured extremities. It is stated by Lassaigne, that in the newly-formed bone, phosphate of lime at first predominates; but that when the new portion is perfected, it contains the same relative proportions of phosphate and carbonate, as those of the original bone.

The bones, including their animal matter, are the most durable portion of the animal fabric; hence the proposal of storing them up as occasional sources of nutriment; for not only is the cartilaginous portion unimpaired, in bones which have been kept dry for many years, but it has even been found perfect, in bones of apparently antediluvian origin. The best mode of extracting the nutritious part of the bone for human food, consists in grinding it fine, and subjecting it, with water, to a heat of about  $220^\circ$ , in a digester; or the earthy part may be removed by hydrochloric acid.

When bones are submitted to destructive distillation, the animal matter which they contain is abundantly productive of ammonia; water and carbonic acid are also formed, and a portion of foetid empyreumatic oil. There remains in the vessel a quantity of charcoal, mixed with the earthy substances, which is, in that state, called *ivory black*. When carbonised bone is freed from phosphate of lime by digestion in dilute hydrochloric acid, the residue is applicable to many useful purposes in chemistry, and in the arts, as a variety of *animal charcoal*.

## CHAPTER IX.

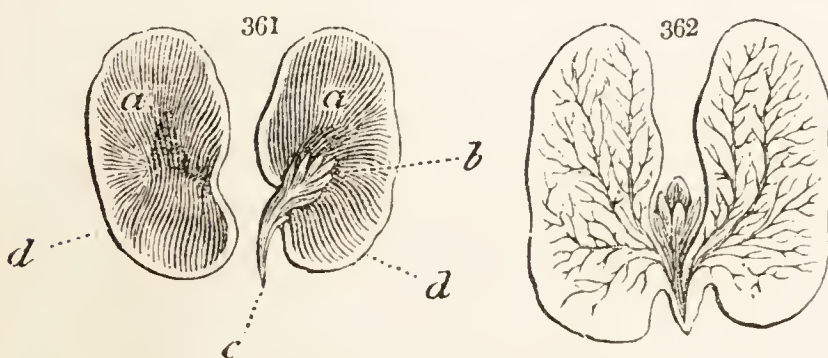
## VEGETABLE AND ANIMAL FUNCTIONS.

HAVING taken a general view of the ultimate and proximate composition of organic products, it now remains to notice the conditions under which they are formed. The importance of the functions of the vegetable creation has already been rendered abundantly manifest; and it has been shown, that without vegetables, animals could not exist. It is in *vegetables* that the elements of inorganic nature, or of the mineral kingdom, are, in the first instance, elaborated into organic compounds, fitted for the sustenance of animal life; they are also the means by which the air is preserved in a fit condition for the respiration of the higher orders of animals, and by which waters are aerated for the breathing of fishes; through them, the elements of the atmosphere, and of the soil, are converted, not only into their own peculiar products, but into those proximate combinations upon which animals subsist, and which are in fact, parts of themselves; so that, it is in vegetables, that the raw materials of the blood, and consequently of the principal organs of animals, are in the first instance produced; leaving to the animal, the comparatively simple task, of weaving them, as it were, into new forms, and ultimately so disposing of them as to restore them to the earth and air, again to sustain new vegetable tribes, and to become parts of future animal creations.

For our knowledge of this wonderful cycle of events, in which decay is seen to be the source of renovation, and destruction, of perpetuity; in which the different kingdoms of nature are shown to be but links of one eternal chain, we are exclusively indebted to *chemical physiology*. The evidence upon which these statements rest, and the experimental data upon which they are founded, are thickly scattered through the preceding pages; so that it only remains now, to notice a few general points bearing upon the functions and phenomena of vegetable and animal life, which we have not elsewhere had an opportunity of adverting to; and first, with respect to the growth, structure, and functions of *plants*.

*Seeds*, from which plants are originally derived, present infinite variety in form and character; without, however, adverting to the minute history of their different parts, we may here refer to the common *garden bean*, as illustrating the general structure of a dicotyledonous seed, and as enabling us to refer generally to their functions and development. This seed, when

the external coverings are removed, is easily separated into two distinct portions, which constitute the bulk of the seed, and which are termed the *cotyledons*; they are represented by *a a* in the annexed cut, fig. 361; between them is seen the *embryo* or *germ*, of which one portion *b*, lying



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between and within the cotyledons, is termed the *plumula*, and the small projecting part *c* is called the *radicle*.

When a seed is placed under favorable circumstances, the different parts begin to *grow*; the membranes burst, the plumula gradually expands, and rises to the surface of the soil, and the radicle puts forth ramifications, and becomes a root. These changes constitute *germination*. The cotyledons, originally insipid and farinaceous, become sweet and mucilaginous, and furnish materials for the early nutriment of the young plant, before its *root* and *leaves* are adequate to their full functions; and vessels are observed for this purpose, as represented in fig. 362. When the root and stem have acquired a certain vigor, the cotyledons either rot away, or become leaves; and the plant then derives its nourishment by the root and leaves, the former collecting materials from the soil, the latter from the atmosphere.

The circumstances requisite for the healthy germination, or growth of a seed, are principally the following:—1. A due temperature, which is always above the freezing-point, and below 100°. 2. Moisture, in due proportion. 3. A proper access of air; the oxygen of which is slowly converted into carbonic acid. The joint operation of these agents also is required: for seeds exposed to air and moisture, but kept below 32°, will not grow, though they are not injured by the low temperature: nor will a seed vegetate without air, though moisture be present, and a sufficient temperature; this is shown by burying seeds deep in the soil; and by the spontaneous vegetation upon newly-turned earth, in which seeds had existed, but through absence of oxygen had been unable to vegetate. Hence, in all cases of tillage, the seeds should be so sown as that the air may have access; in sandy soils this is easily attained; but in clay, the adhesiveness of the material becomes an occasional source of sterility.

The swelling of the cotyledons is occasioned by the absorption of humidity; accordingly, all seeds enlarge in bulk when submerged in water; but those only of *water-plants* will *vegetate* under such circumstances; others require the more free access of air, and grow in the common soil, at depths to which the atmosphere easily finds access, and which moisture easily percolates; but in these early stages of vegetable-development, the soil is of no further use, for the seed will grow upon wet-paper, cloth, stone, or other materials; in short, air, moisture, and heat, are the only external requisites; everything else depending upon the seed itself. During the expansion and softening of the cotyledons, their amylaceous parts become converted into gum and sugar, which are absorbed into the radicle, and contribute to its nourishment, and growth into a root. When seeds are made to germinate in confined portions of air, it is found that they do not alter its bulk, but that a part of its oxygen is converted into carbonic acid; hence, one consequence of germination is a diminution in the relative proportion of carbon in the seed, leaving a comparative excess of hydrogen and oxygen. This evolution of carbon is essential to the growth of the seed, for seeds will not germinate unless free oxygen be present; in hydrogen, nitrogen, and carbonic acid, when aided by moisture, the seed swells at first, but then decays; and in pure oxygen germination is morbidly accelerated; and it is said that certain oxidizing agents, especially the aqueous solution of chlorine, are effective in the restoration of the germinative power to old and dry seeds. All these changes are injuri-



ously affected by *light*; sunshine sometimes kills growing seeds; and even diffused day-light operates unpropitiously; so that in a properly-constituted soil, everything concurs in promoting the healthy functions of the seed; air, moisture, and heat, are duly administered, but the direct influence of light is excluded: darkness seems essential to its perfect development. At first, the *radicle* is most rapid in its growth; the nourishment supplied by the cotyledons going chiefly, if not exclusively to it; it shoots forth its absorptive fibrils, which now take up nutriment from the soil, and feeding upon this, the plumula rises, and puts forth *leaves* and *branches*, the profuse, and even infinite variety of which, may well excite our wonder, and is doubtlessly connected with ends and objects of which we at present are ignorant.

The general phenomena of the development of a seed, are, chemically speaking, the same; but there are extraordinary modifications in the growth of plants derived from those which are *monocotyledonous*, as opposed to those derived from *dicotyledonous* or *polycotyledonous* seeds; the former class includes the *palm tribe*, and the greater proportion of tropical plants; all gramineous and liliaceous plants, likewise belong to it; their growth is *endogenous*, that is, it is the result of additions made *internally*; the latter class comprehends the ordinary forest-trees, and the greater number of our common vegetables; in them the growth is *external* or *exogenous*; and the successive additions to their substance are made upon the *exterior* of the parts from which they proceed.

The *palm-tree* furnishes an instance of endogenous growth: it bears a tuft of leaves at the top of a lofty cylindrical stem, composed of a dense external layer of wood, and increasing in porosity towards the centre; its general texture appears similar throughout; and the distinctions of pith, wood, and bark, are not perceptible in its transverse section: its mode of growth is peculiar; it first forms a circle of leaves, which after having attained a certain size, are succeeded by another circle growing from the interior of the former: these are reproduced annually, each crop exerting an outward pressure upon the ligneous formation of the preceding year, which at length becomes too dense to admit of further distension: the growth of the inner layers is then necessarily directed upwards, so that they each successively rise by distinct stages, always proceeding from the interior; but the stem never increasing in diameter after the consolidation of its exterior layer. A disc of leaves shoots yearly from the new layer of wood, and when these fall off, they leave a circular mark upon the stem; so that the age of the tree may be judged of by the number of these alternations of circular knots. Similar appearances may be observed in grasses.

The section of a *bicotyledonous tree*, or one of *exogenous* growth, exhibits several distinct formations: there is a central *pith*, the structure of which is cellular or spongy, and not tubular, and which is liable to much variation in quantity and character in different plants or trees, and at different stages of their growth: it is surrounded by concentric layers of *wood*, the exterior portions of which are softer than the interior: hence the distinction into *alburnum* or *new-wood*, and *duramen* or *heart-wood*, the former being paler than the latter, which is often brown, and in ebony, black. The wood is enveloped by the *bark*, which consists also of concentric layers, of which the innermost bears the name of *liber*; the



whole is covered by *cellular tissue* and *epidermis*: the bark, like the wood, when more than one year old, is composed of as many layers of cellular integument and woody fibre as it is years old, the former being external, and the latter internal, in each layer, and every layer being formed beneath the previous one, and therefore next the wood: so that the bark is to a certain extent elastic or distensible; but after a time it splits, as in the *elm*, the *cork*, and the generality of European trees; or it peels off, as in the *plane* and *birch*. In the spring of the year, a viscid substance is found between the bark and the wood, which is termed *cam-bium*. Besides these distinct formations which trees of exogenous growth present, the horizontal section of the stem exhibits a number of rays, or lines, proceeding from the pith to the circumference; they are apparently composed of one or more layers of cellular tissue, and are termed *medullary rays*; in longitudinal section they give to many woods a peculiar satiny lustre. As a new layer of wood and bark is formed annually, it is customary to judge of the age of trees by the number of concentric rings which either of them exhibits; but these calculations are open to many fallacies. (See LINDLEY'S *Introd. to Botany*, book i., chap. ii.)

The *cuticle*, or most superficial membrane of plants, is extremely varied in different vegetables, and in different parts of the same plant: it extends over every part of the plant; it allows, by the pores, or *stomata*, of absorption and transpiration, and being generally transparent, at least upon the leaves and flowers, it admits the influence of light. The cuticle varies in texture and appearance in different plants. On the currant and elder tree, it is smooth, and scales off: on the fruit of the peach, and on the leaf of the mullein, it is covered with wool; on the leaf of the white willow it is silky; in several plants it is covered with hair and bristles, which in the nettle are perforated, and contain a venomous fluid: on the plum, and upon many leaves, it is varnished with a resinous exudation, which prevents injury from rain: it is fungous on the bark of the cork-tree; and in grasses, in the equisetum, and especially in different species of the rattan, it is covered with a glassy net-work of silica. This fact first occurred to Sir H. Davy in 1798, and led to experiments by which he ascertained that siliceous earth existed generally in the epidermis of the hollow plants. "It serves," he says, "as a support, protects the bark from the action of insects, and seems to perform a part in the economy of those feeble vegetable tribes, similar to that performed in the animal kingdom by the shell of the crustaceous insects." Silica is also found in the hollow stem of the bamboo, constituting the substance called *tabasheer*. It is to the large quantity of silica existing in grasses, that the glassy character of the products of burned hay and corn stacks is to be attributed.

Under the cuticle, or epidermis, is the *parenchyma*; a soft substance, appearing under the microscope of a honeycombed or hexagonal cellular structure, resulting from the mechanical laws which influence the pressure of soft cylinders.

As the tree grows, the stem and the root both send out their branches or ramifications, and the phenomena of their production are extremely curious and interesting: the branches, and their subdivisions, are generally produced with remarkable regularity, so as to give a defined outline to the shrub or tree, except where unequal exposure to air, light, or heat,

causes one side to expand more luxuriantly than the other: the root, too, in an uniform soil, extends equally on all sides, but various causes likewise interfere with its growth, and it sometimes presents very extraordinary diversions from its usual progress.

I have already noticed the infinitely-varied forms and textures of the *leaves* of plants; their anatomy has been closely investigated by botanists, as well as the mode of their growth or formation; they for the most part exhibit a beautiful skeleton or frame-work of ligneous fibre, supporting a delicate vascular and cellular structure, and are covered by cuticle. The *flowers*, and their parts, are analogous in anatomical structure.

Besides the *cells*, which have been mentioned as constituting a large proportion of the vegetable texture, there also are membranous *tubes* interspersed through their various parts, which exhibit extraordinary varieties in their form, characters, and dimensions; some are simple, others jointed, or spiral, or annular, or perforated; their contents also, as well as those of the cells, are very various; they contain crude or concocted sap, various secretions, or products of vegetation, and air.

The *nourishment of plants* is partly derived from the soil, through the medium of the roots, and partly from the air, by means of the leaves. In spring, before the leaves appear, the roots are chiefly active, and absorb carbonic acid, ammonia, and other matters derived from the soil, and from the decay of the fallen leaves of the preceding autumn. The absorptive power of the root is not merely capillary, but peculiar and vital, and seems to reside in the terminal fibres or *spongioles*, and not in the radicular branches generally; hence the injury inflicted upon the root by careless removal or transplantation; the necessity of carrying with the root a sufficient ball of earth to prevent the abrasion or fracture of the spongioles; and the advantage of growing plants in pots, which are intended afterwards to be removed into the border. The roots absorb some substances more readily than others, but they have no selective power in respect to the most appropriate nutriment; and Saussure has shown that they, in many instances, absorb poisonous substances more rapidly than others. Marcet's experiments have taught us that white arsenic and corrosive sublimate are poisonous to vegetables as well as to animals; and that vegetable poisons are equally active, such as opium and prussic acid, which when applied, even in very dilute solution, to the roots, cause the plant to droop and die. It has been ascertained that the access of a certain quantity of air to the roots of plants is not only not prejudicial, but that it favors the healthy performance of their functions.

The fluids which are absorbed by the roots of plants, constitute the *crude* or *ascending sap*\*; they are circulated in appropriate vessels

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\* The sap of plants is of very various composition, and contains, besides certain proximate vegetable principles, several saline substances, especially the acetates of potassa and of lime: it also often exhibits traces of uncombined vegetable acids. The sap of the elm, beech, hornbeam, and birch, have been examined by Vauquelin (*Ann. de Chim.*, xxxi.): he found extractive

and mucilaginous matter, and acetic acid combined with potassa and lime. The solid matter afforded by their evaporation, yielded an ammoniacal smell, probably owing to albumine: the sap of the birch afforded saccharine matter. Dr. Prout has given some account of the sap of the vine. Its taste is sweetish, and its specific gravity scarcely exceeded that of water. Potassa



throughout the vegetable fabric, being transmitted more copiously to some organs than to others, and contribute to the formation of new parts, and to the composition of their various secretions. Hales, long ago, demonstrated the power with which the sap ascends in its vessels, and endeavoured to account for the rapidity and the direction of its progress; but this phenomenon is still unexplained. A valvular system in the vessels, somewhat similar to that of the veins of animals, was presumed to be efficient in preventing the retrograde motion of the sap: but the well-known fact, that a plant may be inverted, and that the branches may be made roots and the roots branches, subverts such an hypothesis. When the sap has once entered its vessels, it seems invariably to tend (perhaps in the direction of least resistance) towards the *leaves*, which, as regards its chemical changes and elaboration, are certainly most important and essential organs. The quantity of the sap which in many plants, is thus carried upwards from the roots, is very surprising, considering the source whence it must be derived; it may often be abundantly collected by cutting off a branch of a young and thriving tree or shrub, and it is then seen to ooze from the section, flowing over in drops, and running down the stem. The vast evaporation, also, that takes place by the leaves, must be chiefly, if not exclusively, supplied by the roots. Many plants, examined by Woodward, lost, in three months, one hundred times their own weight of water by transpiration. Hales found a sun-flower lose one pound four ounces, and a cabbage one pound three ounces, in twenty-four hours, by this process. This perspiration is said to depend upon the number of the *stomata*, and therefore to be less in evergreens, in which they are few, than in deciduous and herbaceous plants. Whenever the balance between the absorptive power of the spongioles, and the emissive power of the leaves, is disturbed, the plant suffers; as we see by the drooping of the leaves in a warm and dry atmosphere on the one hand; and in a dry soil, on the other.

The *leaves* are the seat of the most important vegetable functions; they are organs of absorption and emission, of nutrition and of digestion. The sap which in its crude state, as it rises from the roots, is extremely dilute, and consists of little else than an aqueous solution of carbonic acid, ammonia, and traces of other salts, is concentrated by evaporation in the leaves,

and ammonia reddened it, and precipitated red flocks soluble in acetic acid. It was rendered slightly turbid by nitrate of silver, subacetate of lead, ferrocyanide of potassium, and oxalate of ammonia. It contained carbonic and acetic acids, and an alkali. (*Ann. of Phil.*, v.) Professor Scherer analyzed the sap of the common maple; it had a milky appearance, and sweet taste. It did not affect litmus or turmeric. It was precipitated by oxalate of potassa, nitrate of silver, and baryta-water. When evaporated, it yielded a salt with base of lime, containing a peculiar acid, which he calls *aceric acid*. (*SCHWEIGER'S Journal*, iv.)

The sap of the rose-tree has been examined by Addams. (*Quarterly Journal*,

iv. 147, N.S.) By the evaporation of 12 ounces he obtained 7·25 grains of residue, consisting of

|  |       |
|--|-------|
| Oxalate of lime . . .                        | 2·900 |
| Acetate of lime . . .                        | 1·097 |
| Acetate of potassa . . .                     | 0·700 |
| Gum and extractive . . .                     | 2·100 |
| Sugar, &c. (soluble in }<br>alcohol) . . . } | 0·100 |
| Loss . . . . .                               | 0·353 |
|  | <hr/> |
|  | 7·250 |

It is, however, almost impossible to collect the sap without the admixture of some other products of the plant, so that the analyses only afford approximations to its real composition.



and receives an addition of carbon from the carbonic acid in the atmosphere; air, and light, and heat, are active in these changes, and the leaves are admirably adapted to such complicated purposes. Their influence in modifying the composition of the sap, and in supplying food to all parts about them, is shown by the mischief which ensues when they are removed; and we have evidence of their emissive, or perspiratory powers, in the watery vapor which they give off, and which sometimes collects in drops; they also occasionally secrete grosser compounds. If we place a healthy leaf between two cold plates of glass, we generally observe that the greatest visible transpiration is from the lower surface, and the organization of the leaf is apparently such, as to render that surface the most apt for the escape of watery vapor: but in some plants the upper surfaces of the leaves are said to be most active; so that probably both the absorptive and excretive power of the leaves varies in different individuals.

One of the most curious and important functions of the leaves is their power of decomposing the carbonic acid which is always present in the air, retaining its carbon, or a portion of it, and emitting oxygen; and to show how important an agent *light* is in inducing these chemical changes, it is found that they only go on under its influence, and that in the dark, they are either inactive, or even deteriorate the air (as we are in the habit of saying,) by the addition of carbonic acid; upon the whole, however, although different plants act very differently in this respect, there can be no doubt that the influence of the vegetable creation upon the atmosphere, is purificative; that is, that part of the carbonic acid produced by animal respiration, and by combustion and other causes, is decomposed by the leaves, and that they evolve more oxygen during the day-time, than carbonic acid during the night. This is well illustrated by Dr. Priestley's experiments on the sprigs of mint already cited (p. lxxv.) and which have been repeated, modified, and verified, by Daubeny, Pepys, Draper, and others: indeed, according to Pepys, the perfectly healthy leaves of the fig-tree, evolve oxygen even during the absence of light. (*Phil. Trans.*, 1843, 329.) We now, also, shall duly appreciate the importance of aqueous vapor, and of carbonic acid, as components of the atmosphere (p. 374), for that the leaves often absorb moisture from the air, is shown by the reviving influence of damp air upon a drooping plant, or of the direct application of water to its leaves. It has also been proved that oxygen is not evolved by plants, except carbonic acid be present in the air. Aquatic plants furnish a striking corroboration of these observations; they decompose the carbonic acid of the air in water, and evolve oxygen during the influence of light; this carbonic acid may be furnished from various sources, but part of it is often derived from the respiration of fishes, and would accumulate to a noxious extent, were it not replaced by the oxygen emitted by the plants; hence it is that fish never thrive in waters which are exempt from vegetation; and that in ornamental vases and basins, in which there are fish, aquatic plants are at the same time desirable. But, although plants will not thrive without access to carbonic acid, its excess is prejudicial, and it has been found to operate as a poison when it exceeds one-twelfth of the atmospheric air; in such proportion, however, it never exists in the free atmosphere. (See a Memoir on the influence of light, and of organic matters, upon the quality



and quantity of the gases of stagnant water by M. A. Morren. *Ann. Ch. et Ph.*, 3ème Sér., i. 456.)

Saussure's experiments upon the functions of the leaves, have taught us the curious fact, that along with the carbon, a portion of oxygen is also absorbed, and this (in the absence of light) from an atmosphere not containing carbonic acid. Fresh leaves, exposed *in the dark* under a bell-glass of air, absorb one portion of oxygen, and convert another into carbonic acid: if afterwards *exposed to the light*, and especially to the direct rays of the sun, they re-absorb the carbon, and give out the whole of the oxygen, gradually restoring the air to its pristine condition. Very succulent leaves (those of the *Cactus opuntia* for instance), absorb oxygen in the dark, and again evolve it in the light: in the course of 30 hours they thus absorbed more than their own bulk, and it could not be extracted from them either by warmth, or by exposing them in the vacuum of the air-pump; though in the sun's rays they invariably emitted it. These properties belong to the leaves of all plants, but the effects vary much in degree in different genera; they are also probably more or less resident in all the *green parts* of vegetables, but are not possessed by the bark or roots. Boussingault has published an elaborate paper in the *Ann. Ch. et Ph.*, (LXIX. 5 and 353,) respecting the absorption of nitrogen by the leaves of plants, but that question is not satisfactorily decided.

It appears indeed from Draper's experiments (*Ann. Ch. et Ph.*, June, 1844), that a portion of nitrogen is always evolved along with the oxygen which plants give out when exposed to light; and that this nitrogen is not merely that which is contained in the pores or cells of the leaf, and which may be abstracted under the receiver of the air-pump, but that it is produced by the decomposition of an azotised principle in the vegetable, and always associated with the decomposition of carbonic acid. Draper's experiments also tend to show, that the evolution of carbonic acid is greatest in that part of the prismatic spectrum where the light is most intense, and that it is not dependent upon the heat of the red end, or upon the chemical powers of the violet end of the spectrum. The latest experiments on the chemical physiology of vegetation are those of Calvert and Ferrand (*Ann. Ch. et Ph.*, August, 1844), who arrive at the following conclusions, viz.: that the decomposition of carbonic acid by plants is proportionate to the intensity and duration of the light to which they are exposed: that the quantity of carbonic acid absorbed is directly as the force of vegetation: and that ammonia exists in vegetables.

The changes which the sap undergoes in the leaves are extremely complicated, and are sometimes manifest in their obvious properties; thus the leaves of some species of *Bryophyllum*, are said to be sour in the morning, tasteless at noon, and bitter at night, reddening litmus at one time of the day and not at another; the flowers of the *Cichorium intibus* are white or blue, according to the intensity of the day-light; and many fruits are observed to be more acid in the morning than in the evening.

The circulation of the sap, as has been before remarked, is involved, as to its cause, in great obscurity, and even the general direction of its progress in the growing vegetable has not been very satisfactorily ascertained; but the researches of Andrew Knight (*Phil. Trans.*, 1801), and

other experimental physiologists, render it probable, that the chief ascent of the sap from the roots to the leaves, is in the vascular system of the *alburnum*, and outer layers of wood; that it is thence transferred into the leaves; and that having there undergone the changes which have been adverted to, it descends chiefly, but not exclusively, by the *liber* or inner layer of bark, giving rise to the secretion of *cambium*, to the formation of new wood, and to the deposition or separation of gum, resin, and other characteristic proximate principles. The proofs of this circulation of the sap are, that if a branch be cut through in the spring, sap will exude more or less from its whole surface, but most copiously from the *alburnum*; if it be cut half through, and a semicylindrical piece removed, the principal exudation of sap upon the upper half, will then be in the inner layers of the bark, and the liquid which there oozes will be different from and more concentrated than that which runs from the outer layers of the wood; as if the *ascending sap-vessels* had been divided in the *alburnum*, and the *descending* in the *liber*; and if a ring of bark be carefully removed from a branch of a young tree early in the spring, the portion above the section will be turgid, and perhaps bear blossom and fruit, indicating symptoms of accumulation of sap, the escape of which from the cut surface is soon prevented by the induration of the inspissated descending sap, and ultimately by the growth of new ligneous matter, the proportion of which is enormous upon the *upper*, as compared with that upon the under line of section. This explains the influence of *ringing* the branches of fruit trees, with a view of rendering them productive; and the difference between the ringed, and the other branches, is often very striking, late in the season, as affecting the fruit, leaves, and general aspect of the plethoric parts.

Plants are for the most part extremely susceptible of impurities in the air that surrounds them; slight modifications, therefore, in the composition of the atmosphere, are more or less prejudicial to their growth; especially when not under the influence of light: thus, although in the sun, a plant will thrive in air containing 8 or 10 *per cent.* of carbonic acid, such excess of that gas is fatal to it in the shade. The experiments of Drs. Christison and Turner upon this subject (BREWSTER'S *Journal*, 1828, and LINDLEY'S *Introduction*, book ii. ch. v.) are very instructive; and instead of being surprised at the injury which plants sustain in the atmosphere of London, lead us to wonder that they are not more generally affected by it. There is no doubt, however, that plants, like animals, vary in regard to the delicacy of their constitutions, and that some are infinitely more susceptible, not only of changes in the temperature and humidity of the air, than others; but are fatally influenced by the presence of foreign matters, which more hardy tribes resist. Dr. Macculloch has given us some curious facts upon this subject. (*Quarterly Journal of Science* for 1829.)

The influence of the *flowers* of plants upon the atmosphere, is probably as various as are their infinitely-varied forms, colors, odors, and composition; even in the light, they invariably deteriorate the air; that is, they convert a portion of its oxygen into carbonic acid, and that, more rapidly than the leaves are found to do, in the dark: the sexual organs of the flower, have been shown by Saussure, materially to influence the destruction of oxygen.



From Berard's experiments on the action of *fruits* upon air (*Ann. Ch. et Ph.*, xvi.), it appears that they, in all cases, tend to the production of carbonic acid, and that this loss of carbon is essential to the ripening of the fruit. When fruits rot, they first change a portion of the surrounding oxygen into carbonic acid, and then liberate the same gas ready formed. He considers gum and lignine as the principles in unripe fruits which chiefly tend to the formation of sugar during their ripening, and has given several analyses of fruits in illustration of these views, a few of which are selected in the following table: the elements of water are also probably concerned in the change.

|                           | CHERRIES. |       | PLUMS. |        | PEACHES. |       | PEARS. |       | APRICOTS. |        |       |
|---------------------------|-----------|-------|--------|--------|----------|-------|--------|-------|-----------|--------|-------|
|                           | Green.    | Ripe. | Green. | Ripe.  | Green.   | Ripe. | Green. | Ripe. | Green.    | Riper. | Ripe. |
| Vegetable }<br>albumine } | 0·21      | 0·57  | 0·45   | 0·28   | 0·41     | 0·93  | 0·08   | 0·21  | 0·76      | 0·34   | 0·17  |
| Coloring }<br>matter.. }  | 0·05      | ..    | 0·03   | 0·08   | 0·27     | ..    | 0·08   | 0·01  | 0·04      | 0·03   | 0·10  |
| Lignine ..                | 2·44      | 1·12  | 1·26   | 1·11   | 3·01     | 1·21  | 3·80   | 2·19  | 3·61      | 2·53   | 1·86  |
| Gum ....                  | 6·01      | 3·23  | 5·53   | 2·06   | 4·22     | 4·85  | 3·17   | 2·07  | 4·10      | 4·47   | 5·12  |
| Sugar ....                | 1·12      | 18·12 | 17·71  | 24·81  | 0·63     | 11·61 | 6·45   | 11·52 | Trace     | 6·64   | 16·48 |
| Malic acid                | 1·75      | 2·01  | 0·45   | 0·56   | 1·07     | 1·10  | 0·11   | 0·08  | 2·70      | 2·30   | 1·80  |
| Lime ....                 | 0·14      | 0·10  | Traces | Traces | 0·08     | 0·06  | 0·03   | 0·04  | Trace     | Trace  | Trace |
| Water....                 | 88·28     | 74·85 | 74·57  | 71·10  | 90·31    | 80·24 | 86·28  | 83·88 | 89·39     | 84·49  | 74·87 |

The evolution of *heat* during the germination of seeds, is well shown by the rise of temperature in the process of malting; and the temperature of the organs of the flower, during the period of their activity, is in some plants, many degrees above that of the atmosphere: these cases of the production of heat must not be confounded with those of fermentation; they are perfectly distinct, especially in the latter case. It appears probable that all plants have a power dependent upon their vitality, of maintaining to a certain extent, an equable temperature; but how far their internal heat can be affected by external causes, has not as yet been satisfactorily ascertained.

I have now briefly enumerated a few of those phenomena of vegetation, in which chemical changes are principally concerned; the whole inquiry is full of interest to the chemical physiologist. Among the *vital powers* of plants, there are some which I have not adverted to, because apparently unconnected with the subject before us; such as the *sleep* of plants; the expansion and contraction of their flowers and leaves, dependent upon the presence or absence of light; their spontaneous and their involuntary motions, as in the *Hedysarum gyrans*, the *Mimosa pudica*, the *Dionæa muscipula*; and the influence of electricity upon the latter.

It has been shewn that carbon, oxygen, hydrogen, and nitrogen, are essential ultimate elements of vegetable products, and it is evident that they derive a part of their carbon and oxygen from the air: their hydrogen and nitrogen are probably acquired chiefly in the form of ammonia. That plants derive much of their nutriment from the soil is obvious from its impoverishment, and from the direct influence of nourishment so

applied; the substances thus taken up, are, or at least may be, very complicated, consisting of a variety of soluble matters, of inorganic, as well as of organic origin; and the rapidity or facility with which they are imbibed depend upon a variety of obscure causes, and partly upon the relative magnitude and absorbent powers of the leaves; for it is, I believe, admitted, that plants with large systems of leaves, absorb less from the soil, than those which are less liberally provided with foliage; and, independent of this, some plants are certainly more voracious and gross feeders than others, thriving in proportion to the richness of the soil, and acquiring odor and flavor from the manure with which they are supplied.

*Manures* are of *vegetable, animal, or mineral* origin. The two former are capable of affording carbon, hydrogen, oxygen, and nitrogen, and they may also yield some of the other principles of vegetables. The mere existence, however, of organic matter in the soil, is not sufficient to constitute it a *manure*; it must be reduced to a state in which it can be absorbed by the roots of a growing vegetable; this is effected by fermentation or putrefaction. Where the vegetable matter is in an inert insoluble form, it will be of no avail unless rendered active and soluble, which is effected either by mixing it with such kinds of animal matter as undergo quick putrefaction, such for instance, as dung, rotten fish, or decaying parts of animals; or, by the operation of alkaline bodies, such as quicklime, &c. When newly-burned lime is strewed over a soil containing inert vegetable matter, it acts upon it, and renders it more or less decomposable, while the lime by absorbing moisture and carbonic acid is slaked, and passes into the state of chalk, which is often a useful addition to the soil, but when limestone contains magnesia it remains caustic and sometimes proves injurious.

It appears, then, from the preceding considerations, that plants derive their nourishment, partly from the air and partly from the soil; and it is probable that their constituent oxygen and hydrogen are furnished in the form of water; that they derive their carbon from carbonic acid, and their nitrogen from ammonia. They also contain certain inorganic constituents, which are furnished almost entirely by the soil. So that water, carbonic acid, ammonia, and certain inorganic substances, may be regarded as constituting the food of plants.

The bulk of a plant, or tree, consists of ternary combinations of carbon, hydrogen, and oxygen, such as wood, starch, gum, sugar; and these may obviously be derived from carbonic acid and water; that is, from the union of the carbon of the carbonic acid, with the hydrogen and oxygen of the water; in which case, the oxygen of the carbonic acid must of course be evolved, inasmuch as in wood, and its congeners, the hydrogen and the oxygen are in the same relative proportions as they exist in water. These substances may, however, also be formed by the union of carbonic acid with the hydrogen of the water; in which case, the evolved oxygen would be derived from the water; in the former case  $\text{CO}_2, \text{HO}$ , would produce  $\text{C, H, O,} + \text{O}_2$ ; and in the latter,  $2\text{CO}_2, 2\text{HO}$ , would produce  $\text{C}_2 \text{H}_2 \text{O}_2 + \text{O}_4$ .

It has been stated that all evidence is in favor of the nitrogen of plants being derived from ammonia; and that ammonia is the common form in which nitrogen is evolved, during the decomposition of azotized



organic matters ; that it passes, in combination with the carbonic acid formed at the same time, into the atmosphere, and is thence abstracted by dew, rain, or snow, and so carried into the soil ; or that it is taken up by humus, clay, and other substances, which mechanically absorb it, and so presented, in aqueous solution, to the root of the plant. It is also furnished, as it were, *directly* to the plant, by the decay of organic matter in the immediate vicinity of the root. "The ammonia," says Liebig, "which is removed from the atmosphere by rain and other causes, is as constantly replaced by the putrefaction of animal and vegetable matters. A certain portion of that which falls with the rain, evaporates again with the water ; but another portion is, we suppose, taken up by the roots of plants, and, entering into new combinations in the different organs of assimilation, produces albumen, gluten, quinine, morphia, cyanogen, and a number of other compounds containing nitrogen. The chemical characters of ammonia render it capable of entering into such combinations, and of undergoing numerous transformations." Liebig then goes on to show, that ammoniacal salts are found in the juices of plants, and to adduce further proofs of the derivation of their nitrogen from that source. (*Organic Chemistry applied to Agriculture, &c.*, p. 80.)

The *inorganic elements of vegetables* are derived chiefly, if not entirely, from the soluble salts of the soil ; and these are either contained in the rocks or strata, from the decay of which the soil originates ; or in the mouldering remains of former crops ; or in substances from time to time added, under the name of *manures*. These inorganic elements are essential to the healthy and vigorous growth of all plants, but they vary in different crops ; in one case earthy sulphates and phosphates may be required ; in another, silicates and salts of the fixed alkalis ; and although in the natural condition of the soil, these may be adequately furnished, yet in an artificial or cultivated state, where the same crop is to be raised year after year, and the produce successively carried away, the soil becomes impoverished, and the crops consequently sickly, unless the abstracted inorganic matters are from time to time replaced.

The particular inorganic matters required for each kind of vegetable, are best judged of by an examination of its *ashes*, and hence the practical value and importance of such analyses ; in some cases the salts of potassa and soda predominate, in others silicates, in others salts of lime, or phosphates, and sulphates. Hence also, the explanation of the well-known fact, that the ashes of each individual plant constitute its effective manure ; that a crop, ploughed into the soil, manures it for the same plant ; that the cuttings of the vine, mixed with the soil, form their best manure ; and also of the efficacy of an interchange of crops, in such a way, that plants requiring much potassa, may be succeeded by other tribes requiring lime ; then by others requiring silicates, phosphates, and so on. When, however, we have once satisfactorily ascertained what the real wants or demands of a crop are, there is no reason why it may not be continuously cultivated upon the same spot, provided the inorganic materials, which are abstracted by it, are duly replaced in the form of dressings and manure. The air and rain will always bring their supply of carbon, hydrogen, oxygen, and nitrogen, in the form of carbonic acid, water, and ammonia, and a fertile soil provides the other requisites ; but to maintain fertility, the necessary constitution of the soil must be maintained ;

and if natural means are inadequate, artificial operations must be resorted to.

The advantages of *fallowing*, *ploughing*, *irrigation*, and some other similar processes, are evidently connected with the reproduction of the inorganic matters of the crop; if the soil is unoccupied, the products of decomposition and decay accumulate; these processes are accelerated by the admission of air; and disintegration; and by the continuous solvent powers of water.

It was at one time supposed that plants could feed upon soluble organic matters; and that the brown extract of a rich soil, or the liquor running from a dung-heap, were in that way available as food for the growing vegetable; and that a great part of their carbon was derived from such sources; but we now know that plants, instead of detracting from, add to the carbonaceous contents of the soil, partly by excretion from their roots, and partly from the autumnal fall and decay of their leaves and fibres; and that although the accumulation of decaying matter which chemists term *humus*, performs an important part in vegetable nutrition, it is not by its direct absorption and assimilation, but by its influence as a source of carbonic acid, which is partly taken up by the juices of the root, and partly evolved into the atmosphere: so that plants, independent of their leaves, can thus receive carbonic acid. It would also appear, from the experiments of Lukas, quoted by Liebig, that the action of humus may, under certain circumstances, be almost exclusively mechanical; that it may, for instance, be replaced by powdered charcoal, a substance in itself inert and insoluble, or at most, only containing small portions of alkaline silicates, but yet administering to the wants of the plant, in consequence of its extraordinary power of condensing carbonic acid, ammonia, and aqueous vapor within its pores. In this way, plants not only grow, but thrive, blossom, and bear fruit, when planted in powdered charcoal, provided the influence of the rain and the atmosphere be not excluded; on the other hand, a plant may die, though its roots are surrounded by the richest mould, if the access of air, and consequent production of carbonic acid, be cut off.

It will be evident, from the preceding sketch of the phenomena of vegetation, that the *functions of plants* consist in the *formation* of a variety of complicated products, out of the comparatively simple materials derived from the air and soil; and that the chief food of plants, independent of certain matters derived exclusively from the soil, may be said to consist of binary compounds of carbon, hydrogen, oxygen, and nitrogen, namely, of carbonic acid, water, and ammonia.

THE FUNCTIONS OF ANIMALS tend, on the other hand, to diametrically opposite effects; their food is either directly, or indirectly, of vegetable origin; consisting exclusively, as far as the graminivorous tribes are concerned, of the complex products of plants; and their functions depend upon the progressive *resolution* of these, into carbonic acid, water, and ammonia: and a plant can no more live upon the ternary and quaternary combinations which are required for the support of animal life, than can an animal, upon the binary compounds of hydrogen and carbon just mentioned.

The researches of Dumas and of Liebig lead us to infer that the food of animals essentially includes two distinct series of proximate principles;



namely, first, those which are *non-azotized*, and consisting of carbon, hydrogen, and oxygen, are principally concerned in maintaining animal temperature, by a species of slow combustion, terminating in the production of carbonic acid and water, which are thrown off by the lungs: these therefore have been termed *aliments of respiration*: and secondly, those which are *azotized*, and which, consisting chiefly of carbon, hydrogen, oxygen, and nitrogen, together with sulphur and phosphorus, are employed for the formation of the principal organs of the body; these have been called plastic *aliments of nutrition*. The *aliments of respiration*, include starch, gum, sugar, lignine, and fat; the *aliments of nutrition* are the proteiniferous products of vegetables, and their congeners, the flesh and blood of animals. The importance of these distinctions will be more evident, if we examine them in relation to the chemistry of the animal functions; and, although these are essentially the same in the graminivorous and carnivorous tribes, we may most conveniently describe them in reference to the less complicated machinery of the latter.

The first operation which the food undergoes is that of *mastication*, and mixture with saliva; and it is then propelled into the stomach, where *digestion*, as it is termed, properly commences. By digestion, the aliments are brought into a state of solution, and converted into an apparently homogeneous pulpy mass, termed *chyme*, the theory of the formation of which has been much simplified by the results of modern research, which have taught us that the proximate principles concerned in the formation of the blood, and which are afterwards to build up the animal fabric, pre-exist in our food; and that the chief end of the function of digestion, is either to subdivide, or to dissolve them. This *solution* of the food has been shown by chemical physiologists to depend upon a species of *fermentation*; “a metamorphosis,” in the language of Liebig, “analogous to fermentation;” or, as Dumas terms it, “a true action of contact, under the influence of an azotized principle resembling diastase.” This *ferment* is probably contained in the saliva, and in the gastric, and pancreatic secretions, for by their aid the same changes may be produced upon food, out of the body, as was long ago shown by Spallanzani, and more lately proved by the experiments of Beaumont, (*On the Gastric Juice and the Physiology of Digestion*), and of Tiedemann and Gmelin (*Ueber die Verdauung*. Heidelberg, 1826). The latter chemists referred the solvent energy of the gastric juice, exclusively to its free acids: but in 1834, Eberlé (*Physiologie der Verdauung*), showed that the presence of a *peculiar organic matter*, in conjunction with the acid, was requisite; that by digesting a portion of the mucous membrane of the stomach, previously washed and dried, in water slightly acidulated by hydrochloric or acetic acid, a liquor was obtained capable of dissolving coagulated albumine, and fibrine, although they were insoluble in the dilute acid, and in the infusion of the membrane of the stomach, when these were used separately. On the other hand, Leuchs found, that saliva possessed the property of dissolving starch, and converting it into sugar; and his experiments have been confirmed by Schwann and Lehmann, and by Mialhe; but whether this property is of any importance in reference to the changes of amylaceous food, seems doubtful.

All experiments then concur in showing, that the solvent powers of the gastric juice depend upon the joint agency of a peculiar *animal principle*,



(which has been distinguished by the term *pepsine*,) and an *acid*, which is probably the hydrochloric, though phosphoric, lactic, acetic, and butyric acids appear to be sometimes present; and it is further probable, that the pepsine derives its activity from being itself in a changing or decomposing condition, for “if the lining membrane of a stomach, perfectly clean and fresh, be infused in water feebly acidulated with hydrochloric acid, the liquid acquires no solvent action on albumine; but if the membrane be exposed to the air for some time, or be left in water for a while, in short, if *decomposition* be allowed to commence, then the infusion, if coagulated albumine or fibrine be placed in it, and the whole kept at the temperature of the body, by degrees effects a perfect solution or digestion.” (LIEBIG.) The resistance of *living* matter to the action of the gastric juice, is illustrated by its non-action upon the organism of the stomach; which, however, after death, is occasionally eaten into holes by it.

In this way, then, the proteiniferous components of food, such as fibrine, albumine, caseine, and glutine, are dissolved by the secretions of the stomach. Starch is probably converted into dextrine and glucose; gum and sugar perhaps undergo some analogous changes, and may possibly tend to the formation of lactic acid; and fatty matters are merely subdivided. To these we must add the liquids which are taken with our food, the principal of which is water; and certain inorganic substances, which are chiefly salts of the alkaline and earthy bases, and oxide of iron. Amongst the former, common salt is pre-eminently important, as appears from its constant presence in the blood, and in many of the secretions; the eagerness with which it is sought after; and the maladies that arise out of its deficient supply; indeed, it is probably the chief source of the hydrochloric acid and of the soda which are found in some of the secretions. Liebig observes, in reference to this subject, that the plants upon which the herbivora feed, cannot grow in a soil destitute of alkalis; but these alkalis are not less necessary for the support of animals than of plants. Soda is found in the blood, and in bile; and potassa exists in the juice of flesh, and in milk; and phosphate of lime, which is essential to the healthy growth of the grasses, is equally essential for the production of bone.

It has been observed that, although animals drink copiously with their food, the consistence of the chyme is not much affected by it; and that by the time it reaches the right, or pyloric extremity of the stomach, the excess of liquid has disappeared. According to Home (*Lectures on Comparative Anatomy*, p. 221), liquids are principally removed by absorbents belonging to the left or cardiac portion of the stomach, and during digestion, there is an imperfect division of the stomach into two cavities, by the contraction of its central bands of muscular fibres. The general opinion now seems to be in favor of the venous absorption of a large portion of the proteiniferous contents of the chyme; so that those important elements of food are, as it were, at once conveyed into the circulation.

We may now trace the chyme into the small intestines, where it soon changes considerably in appearance, by becoming blended with bile, and is ultimately separated into two portions, one of which is white as milk, and is termed *chyle*; the residue, passing on to the large intestines, ultimately becomes *excrementitious*.



The results of the mutual action of the chyme and bile have not been adequately studied, but are no doubt very important. The acid of the chyme is neutralized by the alkali of the bile; the fatty matters of the food are converted into an emulsion; and out of these and the other substances present, the chyle has its origin; it is absorbed by the *lacteals*, which terminate in the common trunk called the *thoracic duct*, and is there mixed with variable proportions of lymph, and poured into the venous system.

There can be little doubt that the bile performs an important part in the change which the chyme suffers in the small intestines; it has been conjectured that its aqueous and alkaline parts are employed as components of chyle, while its other principles combine with the excrementitious portions of the food, and tend to stimulate the intestinal canal towards promoting their propulsion. Whether the bile is absolutely necessary to the formation of chyle, is a question that has not been satisfactorily answered; but its importance is demonstrated by the emaciation that attends its deficiency, and by the disordered state of bowels that accompanies its imperfect secretion. Sir Everard Home, in his *Lecture on the Functions of the Lower Intestines*, (*Lectures*, p. 468,) has offered some curious facts connected with this subject, to which I refer the physiological reader. Brodie found that when the choledoch duct was tied, so as effectually to prevent the flow of bile into the intestine, no chyle was formed; the chyme appeared little altered; and the lacteals, instead of their usual milky fluid, contained a transparent fluid, consisting, apparently, of lymph, and of the more fluid part of the chyme. (*Quarterly Journ.*, xiv. 341.) But Tiedemann and Gmelin assert, that under these circumstances, chyle is formed; and Berzelius also says that chyle is formed, but that it is transparent, because its oil is not saponified: but it must surely be difficult in these cases to distinguish between *transparent chyle*, and certain modifications of lymph; and though it may be possible that, under the absence of bile, the thoracic duct may contain a fluid derived directly from the chyme, and having some general resemblance to chyle, it must be obvious that its composition cannot be that of normal chyle.

Chyle has, at first, the appearance of a milky liquid; but in its passage through certain glands, to the thoracic duct, it acquires a reddish tint, and when taken from the duct itself, is spontaneously coagulable. (*BRANDE, Phil. Trans.*, 1812.) According to Tiedemann and Gmelin, the serum of chyle is reddish yellow; and the coagulum, at first pale, gradually acquires a vermilion tint. They ascribe its white opacity to the presence of globules of fat, the relative quantity of which depends upon the fat in the food; it may be abstracted by ether: it also contains lymph-globules. They found the chyle from the thoracic ducts of horses composed as follows:

|                             | I.     |      | II.    |      | III.   |      | IV.    |
|-----------------------------|--------|------|--------|------|--------|------|--------|
| Water .....                 | 924·3  | .... | 949·8  | .... | 918·03 | .... | 967·9  |
| Coagulum.....               | 17·5   | .... | 4·2    | .... | 7·08   | .... | 1·9    |
| Albumine.....               | 45·5   | .... | 34·3   | .... | 42·08  | .... | 19·1   |
| Fat .....                   | traces | .... | traces | .... | 16·12  | .... | traces |
| Aqueous extract .....       | 7·9    | .... | 8·4    | .... | 11·08  | .... | 9·2    |
| Alcoholic extract and salts | 5·6    | .... | 2·3    | .... | 2·00   | .... | 0·9    |

According to Simon (*Handbuch der Medicinischen Chemie*) the components of the chyle of the horse are

|                                  | I.    |     | II.    |     | III.  |
|----------------------------------|-------|-----|--------|-----|-------|
| Water .....                      | 940.6 | ... | 928.0  | ... | 916.0 |
| Fibrine .....                    | 0.3   | ... | 0.8    | ... | 0.9   |
| Fat .....                        | 1.2   | ... | 10.0   | ... | 3.5   |
| Albumine .....                   | 42.7  | ... | 46.4   | ... | 60.5  |
| Coloring matter of blood .....   | 0.4   | ... | traces | ... | 5.7   |
| Extractive matters and salts.... | 10.1  | ... | 13.7   | ... | 12.8  |

Dr. Prout (*Annals of Phil.*, xiii. 25) obtained the following comparative results from the chyle of two dogs, one fed on vegetable, the other on animal food.

|   | Vegetable Food. | Animal Food. |
|---|-----------------|--------------|
| Water.....                                      | 93.6            | 89.2         |
| Fibrine .....                                   | 0.6             | 0.8          |
| Incipient albumine ? .....                      | 4.6             | 4.7          |
| Albumine with a little red coloring matter..... | 0.4             | 4.6          |
| Sugar of milk .....                             | a trace         | 0.0          |
| Oily matter .....                               | a trace         | a trace      |
| aline matter.....                               | 0.8             | 0.7          |
|   | <hr/> 100.0     | <hr/> 100.0  |

Dr. G. O. Rees, (*Phil. Trans.*, 1842, p. 81,) availing himself of an opportunity of examining the contents of the thoracic duct in a human subject, procured an hour and a quarter after death by hanging, to the amount of six fluid drachms, obtained the following result:

|  |            |
|--|------------|
| Water .....  | 90.48      |
| Albumine, with traces of fibrinous matter .....  | 7.08       |
| Aqueous extractive .....   | 0.56       |
| Alcoholic extractive (Osmazome).....   | 0.52       |
| Alkaline chloride, carbonate, and sulphate, with traces }<br>of phosphate, and oxide of iron ..... | 0.44       |
| Fatty matters.....   | 0.92       |
|  | <hr/> 100. |

The fatty matters possessed the same general characters as those of the blood, except that they did not contain phosphorus, as appeared from their yielding an alkaline, instead of an acid ash, by incineration. The aqueous extractive differed from that of the blood, by giving a ferruginous ash. The salts obtained by incineration from the alcoholic extractive yielded a larger proportion of alkaline carbonate, than those of the blood. Dr. Rees ascribes the white color of the chyle to the presence of opaque white *salivary matter* as one of its constituents; and refers the redness observed in chyle by other analysts, to the accidental presence of blood-globules.

Lastly, it appears from the researches of Bouchardat and Sandras (*Sur la Digestion; Ann. Ch. et Ph.*, 3ème Sér., v. 478), who examined the chyle as well as the chyme of dogs fed upon fibrine, glutine, starch, and sugar, that the composition of the chyle is not so immediately dependent upon the food as preceding physiologists have supposed; for they found it to vary but little in its composition, in animals fed upon amylaceous and upon albuminous substances; but when fed upon fat,



excess of that substance was always contained in it. They therefore regard the chyliferous vessels as chiefly destined for the absorption of fat, previously converted into an emulsion by the action of bile; probably, however, other functions belong to the chyliferous system, and these they thus interpret: When food is taken by a fasting animal, saliva and gastric juice are abundantly secreted: the gastric juice contains hydrochloric and lactic acids, furnished by the decomposition of the chlorides and lactates which abound in the system. Now, as we find free acid on the one hand, we should find free alkali on the other; and hence it appears, that while the stomach prepares the acids, the abdominal glands prepare a chyle for the lacteals and thoracic duct, the alkalinity of which is proportionate to the acidity of the gastric juice. They therefore regard chyle, not as a mere product of the transformation and absorption of food, but as a true secretion, calculated by its alkalinity, which they say is proportionate to the development of acidity in the stomach, to neutralize the acid indispensable for the solution of food, and so prevent the presence of acid in the blood. In this statement, however, the influence of the bile, as a neutralizer, is not sufficiently admitted; and the alkalinity of the contents of the thoracic duct apparently overrated.

*Excrements* consist of such parts of the food as are neither digested nor absorbed; they are blended with more or less intestinal mucus, and biliary matter. During their passage through the intestines they sustain a certain extent of what may be termed putrefactive fermentation, during which gases are evolved, the formation of which is probably partly referable to the air swallowed with the food; these gases are carbonic acid, nitrogen, hydrogen, and carburetted and sulphuretted hydrogen. The solid contents of excrement vary with the quantity and quality of the food, and are generally more abundant after herbaceous or vegetable, than after animal diet. They have been examined by Berzelius (*Lehrbuch*), and by Enderlin (*Ann. der Pharm.*, xlix. 338), and some curious information upon the subject is given by Liebig. (*Chemical Physiology*, &c.) Berzelius examined the excrement after a meal of animal food and bread; it was neither acid nor alkaline; it contained

|  |   |                  |      |   |       |
|--|---|------------------|------|---|-------|
| Water .....                                  |   |                  | 75.3 |   |       |
|  | { | Bile .....       | 0.9  | } | 5.7   |
| Matters soluble in water.....                |   | Albumen.....     | 0.9  |   |       |
|  |   | Extractive ..... | 2.7  |   |       |
|  |   | Salts .....      | 1.2  |   |       |
| Insoluble relics of the food .....           |   |                  | 7.0  |   |       |
| Substances derived from the intestines ..... |   |                  | 12.0 |   |       |
| Mucus, biliary matter, fat, &c. ....         |   |                  |      |   |       |
|  |   |                  |      |   |       |
|  |   |                  |      |   | 100.0 |

The *salts* were specially examined. 3 ounces of fresh excrement left 15.5 grains of ashes, composed of

|  |             |
|--|-------------|
| Carbonate of soda (from lactate) ..... | 3.5 grains. |
| Chloride of sodium.....                | 4.0         |
| Sulphate of soda.....                  | 2.0         |
| Phosphate of magnesia .....            | 2.0         |
| Phosphate of lime .....                | 4.0         |
| <hr/>                                  |             |
| 15.5                                   |             |

Berzelius ascribes the large proportion of phosphate of magnesia to the bread, which he says contained it in notable quantity. He observes that the bones and solids of the human frame, contain less of it than those of graminivorous animals, and that therefore the intestinal absorbents of the former are less inclined to take it up. According to Enderlin, 100 parts of the ashes of human excrement contain

|  |        |
|--|--------|
| Chloride of sodium, and alkaline sulphate .....        | 1·367  |
| Phosphate of soda [ $2\text{NaO}, \text{PO}_5$ ] ..... | 2·633  |
| Phosphate of lime.....                                 | 80·372 |
| Phosphate of magnesia.....                             |        |
| Phosphate of iron .....                                | 2·090  |
| Sulphate of lime .....                                 | 4·530  |
| Silica .....   | 7·940  |
|  | <hr/>  |
|  | 98·932 |

The excrement of the cow has been examined by Einhof and Thær (*Berzelius' Lehrbuch*, Ed. 1831, iv. 261); and more lately, that of the cow and horse, by Boussingault (*Ann. Ch. et Ph.*, Lxxi. 113); they contain upon the average, about 75 per cent. of water. These analyses chiefly, however, refer to the relative proportions of their ashes, and ultimate constituents, and though important in respect to agriculture, are not explicit upon the subject of proximate components. 100 parts of dried horse and cow dung yielded

|                | Horse. |       | Cow.  |
|----------------|--------|-------|-------|
| Carbon .....   | 38·7   | ..... | 42·8  |
| Hydrogen ..... | 5·1    | ..... | 5·2   |
| Oxygen .....   | 37·7   | ..... | 37·7  |
| Nitrogen.....  | 2·2    | ..... | 2·3   |
| Ashes .....    | 16·3   | ..... | 12·0  |
|                | <hr/>  |       | <hr/> |
|                | 100·0  |       | 100·0 |

In reference to *agricultural chemistry*, these subjects are amply discussed by Johnstone (*Lectures*, p. 684). It is obvious that the dung of animals, considered as *manure*, is valuable in two ways; namely, first as a source of ammonia, or nitrogen; and, secondly, as containing phosphates, and other salts. In these cases, however, the urine and excrement are generally mixed; and it is obvious that a great part of the value of the application is due to the former; hence the richness and value of *night-soil*, and similar mixtures. The odor of night-soil renders it in many cases objectionable, and in this country it is generally wasted; but on the Continent of Europe, and more especially in China, it is prudently preserved and efficaciously applied. In China it is mixed up with clay and formed into cakes, which are dried, and sold under the name of *taffo*, and the composition termed *poudrette* is of a similar character. But when night soil is allowed to ferment, and evaporate, although it loses odor, it also loses ammonia, and is much diminished in value. To retain these volatile matters, it is sometimes mixed with mould, sawdust, peat, and similar absorbent substances; sometimes gypsum is used, and dilute sulphuric acid; and in this way, rich and fertilizing composts are obtained, which are comparatively inodorous, but yet retain the principal virtues of the original substance.

Liebig has lately observed, that when certain proteiniferous compounds



are fused with caustic potassa, and the heat continued till hydrogen begins to be evolved, and the greater part of the nitrogen has been expelled in the form of ammonia, the residue, supersaturated with dilute sulphuric acid and distilled, yields an acid liquid having the characteristic odor of human fæces; and he supposes that these odors arise from volatile acids. It is already known, he says, that caprylic acid has the odor of sweat, and valerianic acid that of some modifications of fæcal matter.

It appears then that the proximate elements of our food are dissolved, and to a certain extent modified, in the stomach and small intestines; that the proteiniferous principles are applied to the formation of blood, and to the restoration of those textures which abound in albumine and fibrine; that the fatty substances are conveyed into the circulation, chiefly through the channel of the thoracic duct, to be deposited in different parts of the body, or to be consumed, along with saccharine and amylaceous principles, in maintaining the temperature of the body. With regard to the gelatine of our food, a substance which is *formed* by animals, inasmuch as it does not constitute a proximate principle of vegetables, it is obvious that inasmuch as it differs in composition from proteine, it cannot, like that substance, be directly applicable to the formation of fibrine and albumine. Yet, when we feed upon articles abounding in gelatine, as upon jellies and strong soups, it is not found either in the urine or fæces, and therefore must have served some purpose in the animal economy. So also when dogs are fed upon bones, the phosphate of lime of the bone is voided, (forming the earthy excrement formerly called *album Græcum*,) while the gelatine entirely disappears.

It has been suggested by Liebig, that the gelatine of our food may possibly be applied to the formation of cellular tissue, membrane, cutis, and cartilage; and that it may serve for the reproduction of such parts of those tissues as have been wasted.

Inasmuch as fatty matters may be traced passing directly from our food into the blood, and as more or less fat is contained in all our common articles of nutrition, in bread, milk, meat, eggs, &c., and often eaten in no inconsiderable quantity in its pure state, as in oil, butter, suet, marrow, &c., it has been assumed by some chemical physiologists, that animals have no power of *producing* or *forming* fat; and that all that is found in their tissues, is taken in with their food, and merely deposited in the different organs and parts in which it occurs; and calculations have been made in reference to this hypothesis, showing the possibility of the direct derivation of the fat in graminivora, from the vegetables which sustain them. And in the fattening of cattle and other animals, the influence of the quantity of the fat in the food is sufficiently obvious. On the other hand it is assumed, and with great appearance of truth, that the accumulations of fat which ensue, under certain conditions, in the animal system, indicate a power of *forming* it. The bee, it is argued, produces wax, which is a species of fat, though fed upon pure sugar; and a goose, tied up, and fed with farinaceous food, destitute, or nearly so, of fat, shortly augments by several pounds in weight, from the accumulation of fat. According to Liebig, the chief sources of fat are starch and sugar, the composition of which is such, as to yield fat by deoxidation. If from starch,  $C_{12}H_{10}O_{10}$ , we take 9 atoms of oxygen, there remain  $C_{12}H_{10}O$ , which is one of the empirical formulæ for fat; or, if we abstract 1 atom of

carbonic acid, and 7 atoms of oxygen  $[CO_2, O_7]$  from starch, the remainder, which is  $C_{11} H_{10} O$ , represents another formula for fat. He also shews, that in the absence of amylaceous matters, fat may be derived from proteiniferous compounds, by an analogous process of deoxidation. It is, indeed, self-evident that fat may be formed in the living body, and that it may be derived from starch and its analogues, in the same way as gelatine may be derived from albumine and its analogues; and although both fat and gelatine may, to a certain extent, be derived directly through our food, it is probable that both those substances are also occasionally formed in the animal system.

Having stated thus much respecting the nature of animal food, and of the changes which it undergoes in the digestive organs, we may now trace its further metamorphoses, in reference chiefly to the phenomena of *respiration*.

The difference between *arterial* and *venous* blood has been adverted to in a previous section: the former is of a florid red color, and circulates in the *arteries*; it is contained in the left ventricle of the heart, and thence carried by the *aorta*, and its ramifications, to every part of the body, tending to reproduction and secretion: it afterwards enters the *veins*, which arise from the extremities of the arteries, and form accompanying branches and trunks, ultimately uniting in the *venæ cavæ*, which pour their contents into the right auricle of the heart; the venous blood is thence propelled into the right ventricle, from which the pulmonary artery arises, transmitting it through the lungs, whence it is returned by the pulmonary vein into the left auricle, which transmits it to the left ventricle, from which issues the aorta as aforesaid. So that the right cavities of the heart receive venous blood, and transmit it through the lungs, whence it returns to the left side of the heart, in the arterial state. In the lungs the blood is infinitely subdivided, and spread over a very large surface, in vessels so delicate as to admit of the operation of the atmospheric air contained in their cells; it enters the pulmonary structure in the *venous* state by the *pulmonary artery*, and returns in the *arterial* or *aërated* state, by the *pulmonary vein*. It now remains to examine the changes which the blood undergoes during pulmonary circulation.

*Respiration* is the process of receiving a quantity of air into the lungs, whence, after having been retained a short time, it is again expelled in the action of expiration: and, if now examined, a portion of its oxygen is found exchanged for carbonic acid, and it is more or less loaded with aqueous vapor. The nitrogen of the air probably remains passive, although from Dr. Edwards's experiments there appears to be some doubt upon this subject, for sometimes it appeared to be emitted, and sometimes absorbed in small quantities by the blood. (*De l'Influence des Agens Physiques sur la Vie*, 1824.) Upon the whole, it would seem probable, that although a small quantity of nitrogen may occasionally, at least, be emitted by the blood, that element is not *absorbed*, inasmuch as there appears to be more nitrogen conveyed by our food into the body, than is eliminated from it in the excretions.

Obvious circumstances render it very difficult to ascertain the exact quantity of air taken into the lungs at each natural inspiration, as well as the number of respirations made in a given time; the former is, perhaps, about 15 or 16 cubic inches; and the latter about 20 in a minute.



It has been supposed that the air suffers an actual diminution of bulk, but the experiments that have been adduced to determine its absolute amount are much at variance. Dr. Edwards thinks that a portion of air disappears, but that it is very variable in its amount. (Bostock, *Physiology*, ii. 101.) Davy long ago suspected that nitrogen was taken up by the blood, and that the volume of carbonic acid evolved, always fell short of that of the oxygen absorbed. (*Researches on Nitrous Oxide*, &c., 1800, p. 448.) This latter opinion appeared sanctioned by the experiments of Despretz. (*Ann. Ch. et Ph.*, xxvi. 337.) According to Valentin and Brunner, (Löwig, i., 683,) for each volume of oxygen which disappears, 0.9157 vol. of carbonic acid is given out; and as 1 volume of carbonic acid gas includes 1 volume of oxygen, it follows that about one-tenth of the latter gas is concerned in the oxidizement of hydrogen.

The quantity of carbonic acid emitted at each expiration, varies at different periods of the day, and in different individuals; it appears at its maximum during digestion, and at its minimum in the morning, when the stomach is empty, and when no chyle is flowing into the blood. Dr. Prout states that fermented liquors and vegetable diet diminish the proportion of carbonic acid, and that the same thing happens when the system is affected by mercury.

The air expired after a single inspiration has generally been regarded as containing, on an average, 3.4 per cent. of carbonic acid; Allen and Pepys, however, in their *Essay on Respiration*, (*Phil. Trans.*, 1808), have estimated it at about twice that quantity; it amounted, in their experiments, to between 26 and 27 cubic inches per minute, a considerable quantity, when we reflect upon the comparative proportion of carbon existing in our food, and the other means of escape which that element has from the body.

The following table shows the results of several experimentalists in reference to the average quantity of air required for respiration, and of carbonic acid produced by an adult man. (LIEBIG'S *Animal Chem.*, p. 283.)

|                           | Of oxygen required<br>in 24 hours. |        | Carbonic acid produced<br>in 24 hours. |         | Weight of<br>evolved Carbon. |  |
|---------------------------|------------------------------------|--------|--|---------|------------------------------|--|
|                           | Cub. inches.                       | Grains | Cub. inches.                           | Grains. | Grains.                      |  |
| Lavoisier and Seguin .... | 46037                              | 15661  | 14930                                  | 8584    | 2820 Fr.                     |  |
| Menzies .....             | 51480                              | 17625  | ...                                    | ...     | Eng.                         |  |
| Davy .....                | 45504                              | 15751  | 31680                                  | 17811   | 4853                         |  |
| Allen and Pepys.....      | 39600                              | 13464  | 39600                                  | 18612   | 5148                         |  |

It is stated by Mr. Gregor, in a communication to the British Association, that the healthy average of carbonic acid amounts to 3.5 per cent., but that it is increased to 6 or 8 per cent. in the first stage of small pox, and in measles and scarlet fever to 4 or 5 per cent. He says that in some cutaneous affections there is also an increase, but none in diabetes. According to Andral and Gavarret, (*Ann. Ch. et Ph.*, Juin, 1843,) the quantity of carbonic acid emitted in a given time from the lungs, varies considerably with the age, sex, and constitution of the individual; they state, that between the age of 16 and 40, the male exhales nearly twice as much as the female. That in males, the quantity of carbonic acid increases, from 8 to 30 years of age; that it then decreases, to extreme old age, and may thus be reduced to the same standard as at the age of

10 years. That in males, the exhalation of carbonic acid sustains a remarkable increase, and in females a decrease, at the age of puberty, and that in all cases, the production of carbonic acid is greatest in the strongest, and most robust and muscular persons. The following are abridgments of two tables given in the memoir quoted:

| MALES.         |   |         | FEMALES.         |   |         |
|----------------|---|---------|------------------|---|---------|
| Age.           | Grammes<br>of Carbon<br>burned<br>per hour. | Grains. | Age.             | Grammes<br>of Carbon<br>burned<br>per hour. | Grains. |
| 8 to 15 ....   | 7.4 =                                       | 113.96  | 10 to 15.....    | 6.4 =                                       | 88.56   |
| 15 to 20 ....  | 10.8 „                                      | 166.32  | 15 to 45.....    | 6.4 „                                       | 88.56   |
| 20 to 30 ....  | 12.2 „                                      | 187.88  | 38 to 82.....    | 7.4 „                                       | 113.96  |
| 30 to 40 ....  | 11.0 „                                      | 169.40  | During pregnancy | 7.9 „                                       | 120.8   |
| 40 to 50 ....  | 9.4 „                                       | 144.76  |                  |   |         |
| 50 to 60 ....  | 11.0 „                                      | 169.4   |                  |   |         |
| 60 to 70 ....  | 11.0 „                                      | 169.4   |                  |   |         |
| 70 to 102 .... | 6.9 „                                       | 96.26   |                  |   |         |

We have also, in reference to the quantity of carbonic expired in the course of 24 hours, some very precise experiments by Scharling, (*Ann. der Pharm.*, XLV. 214; *Ann. Ch. et Ph.*, 3ème Sér., viii. 478,) shewing that it is liable to much variation. He found it greatest after meals and violent exercise; and he estimates it at about one-fifth less during sleep than when awake. The following are the mean results of some of his experiments; he allows 7 hours of sleep for adults, and 9 hours for children.

| Sex.         | Age. | Weight of the Indi-<br>viduals, |       | Weight of Carbon<br>evolved in 24 hours, |        | Weight of<br>Carbon in<br>1 hour, |
|--------------|------|---------------------------------|-------|--|--------|-----------------------------------|
|              |      | In lbs. avoirdupois.            |       | In grains.                               |        | In grains.                        |
| Males .....  | 9    | ....                            | 49    | ....                                     | 2048   | 85.3                              |
|              | 16   | ....                            | 130   | ....                                     | 3449   | 143.3                             |
|              | 28   | ....                            | 184   | ....                                     | 3696   | 154.0                             |
|              | 35   | ....                            | 147   | ....                                     | 3388   | 141.2                             |
| Females .... | 10   | ....                            | 51    | ....                                     | 1925   | 80.2                              |
|              | 19   | ....                            | 126   | ....                                     | 2556   | 106.5                             |
| Average 17.8 |      |                                 | 114.5 |  | 2843.6 | 118.4                             |

It appears, therefore, upon these data, that the average quantity of carbon evolved in the 24 hours, amounts to about 120 grains per hour: the average deduced from the experiments of Andral and Gavarret is about 140 grains per hour. If we take the mean of these results, = 130 grains per hour, it gives 3120 grains as the weight of carbon evolved from the lungs in 24 hours; that is, somewhat more than 7 ounces avoirdupois; an estimate not widely different from that long ago assumed by Dumas.

In respect to the quantity of carbonic acid produced by other animals, it appears from the experiments of Boussingault, (*Ann. Ch. et Ph.*, LXXI. 135,) that a horse, moderately fed, gives off from the lungs nearly 80 ounces of carbon daily, and a cow upwards of 70 ounces.

The aqueous vapor contained in the expired air is probably partly secreted by the exhalants distributed over the surface of the air-vessels of the lungs, partly derived from the humidity of the mouth, fauces, and trachea, and partly evaporated from the blood. Attempts have been



made to estimate its quantity, but without success; perhaps the nearest estimate is about 3 grains per minute; it is certainly liable to much variation. It is estimated by Menzies to amount to 2880 grains in the 24 hours; by Abernethy, to 4320; by Thomson, to 9120; by Hales, to 9792; and by Lavoisier, to 13,704 grains. The large and variable quantity of water taken into the system with the food, and the great variations in the proportion of water which passes out of the body with the urine and fæces, and by the skin, render it very difficult to form even an approximate estimate of that which escapes in the state of vapor from the lungs, or to form any correct notion of the quantity which may possibly be derived from the combustion of hydrogen.

The function of *perspiration* must also be considered as connected with an alteration of the circulating fluid, for moisture, carbonic acid, and minute quantities of acid, and of saline and animal matter, among which are acetic or lactic acid, acetate and hydrochlorate of ammonia, and chloride of sodium, are evacuated by the cutaneous vessels. The quantity of humidity is sometimes very considerable, especially during exercise, and in warm weather, and it probably contributes materially to diminish the temperature of the body; a portion of water, however, is at all times passing off by the skin, as may be seen by putting the hand into a dry and cold glass, which soon becomes dimmed by the condensation of vapor: this is termed *insensible perspiration*. According to Anselmino, as quoted by Tiedemann, and by Berzelius, the *dry residue* of human perspiration contains

|   |    |
|---|----|
| Saline matters, chiefly calcareous, and insoluble in water and in alcohol....                             | 2  |
| Substances soluble in water, but insoluble in alcohol, comprising animal matter and sulphuric salts ..... | 21 |
| Common salt and extractive matter soluble in dilute alcohol .....   | 8  |
| Extractive matter, lactic acid, and lactates, soluble in anhydrous alcohol....                            | 29 |

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 100

The relative proportion of solid matter to that of the water, in sweat, varies according to Thenard, from 0.5 to 1.25 per cent. (*Ann. de Ch.*, Lix. 262.) Some peculiar matters are occasionally thrown off by the skin, giving rise to *colored perspiration*. I have heard of a case in which a man's linen was thus tinged blue; and Dr. Williams mentions the case of a woman whose perspiration, when profuse, dyed the clothes on some parts of her person, particularly the wrists and neck, of a bright crimson color, but without any marks of blood; this was supposed by Dr. Prout to be caused by sulphocyanide of iron.

Different animals require very different quantities of oxygen for the purposes of respiration. Man, and warm-blooded animals, consume the largest quantity; the amphibious tribes not only require less, but can breathe in an atmosphere which will not support the life of the former; and many insects take such small quantity, as sometimes to have been supposed capable of living without air, which is not the case. In the production of carbonic acid, all animals agree; and, consequently, the nature of the deterioration suffered by the air is similar throughout the animal creation.

Fishes breathe the air which is dissolved in water; they therefore

soon deprive it of its oxygen, the place of which is supplied by carbonic acid; this is in many instances decomposed by aquatic vegetables, which restore oxygen, and absorb the carbon; hence the advantage of cultivating growing vegetables in artificial fish-ponds. It has been ascertained by Biot, and verified by others, that the air-bladders of fish that live in very deep water, are filled with a mixture of oxygen and nitrogen, in which the former greatly preponderates; but in fish that are taken near the surface, the nitrogen is most abundant. In the *Trygla lyra*, always caught in very deep water, the air-bladder contained 87 per cent. of oxygen: in the carp and roach, according to Fourcroy and Priestley, the air-bladder contains little else than nitrogen. (BIOT, *Mémoires d'Arcueil*. On the Respiration of *frogs*, see MARCHAND, *Ch. Gaz.*, April, 1845.)

It has been above stated, that the whole of the venous blood is propelled through the vessels of the lungs, where it is subjected to the action of the air; the chyle is of course carried along with it, and when it returns by the pulmonary vein to the left side of the heart, it has undergone a considerable change in appearance, having lost its dingy color, and acquired a fine florid red; the chyle also has become perfect blood. The change of color depends upon the action of the air, which takes place through the thin coats of the circulating vessels, and the chief end thus attained is the removal of the carbonic acid from the venous blood. The only chemical difference, then, which can be satisfactorily detected between arterial and venous blood, is the existence of a certain excess of carbon, or of carbonic acid, in the latter; when this is abstracted, and oxygen substituted for it, the blood is fitted for the renovation of parts, for the formation of secretions, and for the sustenance of life by its action on the cerebral system; for although the heart does not directly refuse to circulate venous blood, torpor ensues when blood, not aërated, passes into the vessels of the brain.

The precise manner in which the oxygen is absorbed in the lungs, and the conditions under which the carbonic acid is evolved, are questions which have engaged much of the attention of chemical physiologists, and upon which various opinions have been put forth. According to Liebig (*Chemical Physiology and Pathology*, 265, and *Turner's Chemistry*, edited by Liebig and Gregory, p. 1318), the *blood globules* are the principal agents by which these changes are effected, being, as it were, the carriers of the oxygen into the system, and of the carbonic acid out of it: they are supposed to possess the power of absorbing oxygen in the lungs, conveying it to all parts, giving it up to the particles of the tissues undergoing change, and there receiving carbonic acid in its stead. The iron in the blood globules was at one time supposed to be the element upon which their functions essentially depended; it was assumed to exist in the venous globules in the state of protocarbonate, and in the arterial globules in the state of peroxide; the protocarbonate, in consequence of the evolution of carbonic acid and the absorption of oxygen, becoming converted in the lungs into peroxide; and the peroxide becoming deoxidized and passing into protocarbonate, in the capillaries of the venous system. It has also been assumed that the carbonate of soda in the blood, became bicarbonate in the venous system, and reverted to the state of carbonate, after having passed through the lungs. But it is now stated, upon the authority of Enderlin, referred to by Liebig, that



there are no carbonates in the blood, and that the alkalinity, and other properties of the blood, originally ascribed to carbonate of soda, are due to *phosphate of soda*,  $2\text{NaO}, \text{HO}, \text{PO}_5$ , a salt which has an alkaline reaction, and which absorbs twice as much carbonic acid as carbonate of soda, and again gives off the whole of it. No salt, according to Liebig, is so well adapted for this function; and it is, he observes, truly remarkable, that while both phosphate of soda and phosphate of potassa exist in the food, the former alone should occur in the blood; "and this is especially wonderful, when we consider that the juice of *flesh*, which is only separated from the blood by thin membranes, permeable to liquids by endosmose and exosmose, contains much phosphate of potassa, and little or no phosphate of soda: it is evident that the vessels or cells must possess, in their peculiar membranes, a power of selection, or of allowing some salts to pass in one direction only, and others in the opposite." He then goes on to show, that the tendency of phosphate of potassa is to form an acid salt  $= \text{KO}, 2\text{HO}, \text{PO}_5$ ; whereas that of phosphate of soda is to form an alkaline salt  $= 2\text{NaO}, \text{HO}, \text{PO}_5$ ; and that those phosphates cannot therefore replace each other, in the blood; and he infers that where phosphate of potassa is contained in the food of animals, phosphate of soda is derived from the mutual action of phosphate of potassa and chloride of sodium. (*Researches on the Chemistry of Food*, 1847, p. 110.)

*Animal heat.* The power of producing heat appears to belong to all animals, though to some in a very inferior degree. The higher orders of animals always maintain a temperature of about  $100^{\circ}$ ; it varies a little in different parts of the body, the extremities and surface being a degree or two colder than the interior vital organs. This temperature is probably very little affected by external circumstances, a hot or cold atmosphere producing no corresponding change in the heat of the circulating blood.

When the chemical changes that take place during respiration had been inquired into, it was supposed that the conversion of oxygen into carbonic acid was the principal cause of the rise of temperature; and as the heat of the lungs does not exceed that of other parts, it was asserted that the air was absorbed by the blood, and that the production of carbonic acid, and consequent evolution of heat, took place gradually during the circulation in the capillaries. To these opinions objections have from time to time been urged by different physiologists. Sir B. Brodie (*Phil. Trans.*, 1812), found that the heart was capable of retaining its functions for some hours, and of carrying on circulation, in a decapitated animal, (and consequently independent of the influence of the brain,) when respiration was artificially carried on. Under these circumstances it was observed, that although the change of blood from the venous to the arterial state, arising out of loss of carbonic acid, was apparently perfect, heat was not generated, for the animal cooled regularly and gradually down to the atmospheric standard; so that circulation went on, there was the change of oxygen into carbonic acid, and the alteration of color in the blood, and yet heat appeared not to be generated. In reference to this subject Dr. Turner (*Elem. of Chemistry*, 5th edition, 983,) observed that were these experiments rigidly exact they would lead to the opinion that no caloric is evolved by the mere process of arterialization; this inference however cannot be admitted for two reasons; first, because

other physiologists, in repeating the experiments of Brodie, have found that the process of cooling is *retarded* by artificial respiration; and secondly, because it is difficult to conceive why the formation of carbonic acid, which uniformly gives rise to increase of temperature in other cases, should not be attended, within the animal body, with a similar effect. It may, hence, be inferred, that this is *one* of the sources of animal heat. It is certain, however, that the heat of animals cannot be maintained by the sole process of arterialization. Consistently with this fact, the researches of Despretz prove, in opposition to the results obtained by Lavoisier and Crawford, that a healthy animal imparts to surrounding bodies, a quantity of heat considerably greater, than can be accounted for by the combustion of the carbon thrown off during the same interval from the lungs, in the form of carbonic acid. (*Ann. Ch. et Ph.*, xxvi.) The experiments of Dulong also show that the fixation of oxygen is not adequate to account for the temperature of hot-blooded animals. (*Ann. Ch. et Ph.*, 3ème Sér., i. 440.)

In Brodie's experiments upon decapitated animals, it was found that a period was also put to the *secretory functions*; and it has been observed by other physiologists, that if the nerves that supply any of the glands are injured or divided, there is a corresponding change or suspension of their secretion. Electricity has sometimes been supposed to have some connexion with the nervous influence, and the fact of some of the secretions being alkaline, while others are acid, (corresponding to negative and positive influence,) has been adduced in favor of the supposition (*Phil. Trans.*, 1809, p. 385); but experiment has gone little way to sanction such a notion; and assuming it to have been proved that the *nervous influence* contributes to the generation of heat in animals, and that it presides over the phenomena of secretion, as well as of sensation and voluntary motion, neither the actual cause of this influence, nor the mode in which it operates, have been ascertained.

If we now contrast the functions of animals with those of vegetables, we cannot but be struck by the admirable adjustments which regulate them, and by which they are rendered mutually subservient and dependent. We have shown that the food of the vegetable kingdom is principally administered to it in the form of water, carbonic acid, and ammonia; that these substances are decomposed in the plant, and that their ultimate elements, namely, carbon, hydrogen, oxygen, and nitrogen, together with certain substances derived from the soil, among which phosphorus and sulphur, potassa and soda, lime and magnesia, chlorine and iron, are the most essential, are elaborated by the vegetable organism into the proximate principles, or in other words, into the food of animals; namely, into all the modifications of proteine; into sugar, gum, and starch; and into fat. In the animal system, on the other hand, these proximate principles are successively resolved into more simple forms, and ultimately into the very carbonic acid, ammonia, water, and inorganic products, upon which plants feed. Carbonic acid and water are copiously thrown off by the lungs; the kidneys secrete urea, which readily passes into carbonate of ammonia; and the inorganic substances are found in the excrements. In the living animal these changes are essential to the continuance of the vital functions, and the vital functions to them; but similar changes go on after death; so that the fabric, deprived of its



reproductive requisites, vanishes into the gaseous and solid products which have just been enumerated.

These respective attributes of the Vegetable and Animal Kingdoms, have been well contrasted, by Dumas and Cahours. (*Ann. Chim. et Phys.*, 3ème Sér., vi. 386.)

| VEGETABLES                                | ANIMALS                                    |
|---|--|
| <i>Produce</i> proteiniferous substances, | <i>Consume</i> proteiniferous substances,  |
| „ fatty matters,                          | „ fatty matters,                           |
| „ sugar, starch, gum.                     | „ sugar, starch, gum.                      |
| <i>Decompose</i> carbonic acid,           | <i>Produce</i> carbonic acid,              |
| „ water,                                  | „ water,                                   |
| „ ammonia.                                | „ ammonia.                                 |
| <i>Evolve</i> oxygen.                     | <i>Absorb</i> oxygen.                      |
| <i>Absorb</i> heat and electricity.       | <i>Evolve</i> heat and electricity.        |
| Constitute an apparatus of <i>reduc-</i>  | Constitute an apparatus of <i>oxidize-</i> |
| <i>tion</i> .                             | <i>ment</i> .                              |
| Are <i>stationary</i> .                   | Are <i>locomotive</i> .                    |

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## APPENDIX

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### I. ENGLISH WEIGHTS AND MEASURES.

IN England we still retain a merely arbitrary system of weights and measures, originally settled in times when no regard was paid to the advantage of simple numerical ratios either between the different measures themselves, or between any one of them and a natural standard, had such a standard been known. Even between the various units of the same kind of magnitude, the ratios are highly inconvenient, involving such numbers as 7 and 11 for instance; but between the units of magnitude of different kinds, no sort of connexion seems to have been attempted; so that, till within a few years, the measures of *length*, *volume*, and *weight*, formed three distinct and independent systems, between the units of which, it was necessary, for scientific purposes, to find an approximate ratio, as between different natural standards; and though the measures of *capacity* have now been remodelled, and made to bear a simple relation to those of *weight*, yet the relation of either of these to the measures of *length*, and of these again to a natural standard, can only be expressed by very complex and purely arbitrary numbers.

The natural standard to which all our measures are referred, depends on the time of the earth's rotation, and the amount of gravitation at a given point of its surface; both which elements have been proved by astronomy to be invariable. The time of the earth's rotation is subdivided alike in all civilized countries, into 86,400 seconds. It has therefore been made a law in this country, that the distance from the point of suspension to the centre of oscillation, of a pendulum which, when placed in vacuo, in the latitude of London, and at the level of the sea, makes 86,400 vibrations in a mean solar day, shall be taken as 39.1393 English inches. Accordingly, the platinum yard scale adopted for a national standard, measures at the temperature of 62° Fahr., 36 such inches.

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#### WEIGHTS.

Weights are connected with the above standard, by the enactments that 277.274 cubic inches shall constitute an *Imperial Gallon*; and that



the weight of this volume of pure water, weighed in air of 30 inches pressure, at 62°, shall be taken as 10 *avoirdupois pounds*, or 70,000 *grains*.

The two systems of weights called *Troy* and *Avoirdupois*, have no common integer except the *grain*. Though the names *pound*, *ounce* and *drachm* are common to both systems, they denote different quantities in each.

The English *troy pound* is subdivided into twelve ounces, and each ounce is equal to 480 grains. The subdivisions of the troy ounce, called *Apothecaries' weight*, are into 8 drachms, each drachm into 3 scruples, and each scruple into 20 grains. The troy ounce is also sometimes divided into 20 penny weights, of 24 grains each. These are the weights generally employed; but for philosophical purposes, ambiguity is most easily avoided, by employing the *grain* as integer: and the Laboratory should be provided with good sets of weights, from 1000 grains downwards; the grain should be decimally subdivided into tenths, hundredths, and thousandths.

The standard of most articles bought and sold in common life, is the *avoirdupois pound*, which is equal to 7000 grains, and is divided into 16 ounces, of 437·5 grains each. The *avoirdupois ounce* is legally divided into 16 drachms, of 27·34375 grains each; but this division is rejected in all ordinary cases, in consequence of the confusion likely to result between the troy and *avoirdupois drachm*, so that the term *drachm* is almost exclusively employed to denote the *eighth part of a troy ounce*, or 60 grains.

In the following Tables are shown the subdivisions of the English troy and *avoirdupois pounds*, and their correspondence with the French *gramme*.

#### TROY WEIGHT.

| Pound. | Ounces. | Drms. | Scruples. | Grains. | Grammes.       |
|--------|---------|-------|-----------|---------|----------------|
| 1      | = 12    | = 96  | = 288     | = 5760  | = about 372·96 |
|        | 1       | = 8   | = 24      | = 480   | = 31·08        |
|        |         | 1     | = 3       | = 60    | = 3·885        |
|        |         |       | 1         | = 20    | = 1·295        |
|        |         |       |           | 1       | = 0·06475      |

#### AVOIRDUPOIS WEIGHT.

| Pound. | Ounces. | Drms. | Grains.    | Grammes.       |
|--------|---------|-------|------------|----------------|
| 1      | = 16    | = 256 | = 7000     | = about 453·25 |
|        | 1       | = 16  | = 437·5    | = 28·328       |
|        |         | 1     | = 27·34375 | = 1·7705       |

The larger units of this system are multiples of the pound by 7, thus

| Ton. | Hundredweights. | Quarters. | Stone. | Cloves. | Pounds. |
|------|-----------------|-----------|--------|---------|---------|
| 1    | = 20            | = 80      | = 160  | = 320   | = 2240  |
|      | 1               | = 4       | = 8    | = 16    | = 112   |
|      |                 | 1         | = 2    | = 4     | = 28    |
|      |                 |           | 1      | = 2     | = 14    |
|      |                 |           |        | 1       | = 7     |

The very peculiar division of the hundred-weight may possibly have been chosen for the following advantage; that every smaller number of pounds can be weighed by using a series of weights altogether equal to 112 lbs., and no two of which are similar. This arises from 28, the number of lbs. in a quarter, being a *perfect* number, *i.e.* equal to the sum of all its integral divisors; a property so rare, as to be possessed by only ten numbers below a trillion, or 1,000000,000000,000000.

### MEASURES OF VOLUME.

Previous to the introduction of the present *Imperial Measure*, as it is termed, *Wine Measure* was generally used for measures of capacity: the *wine pint* corresponds to 28·875 cubical inches of water, at the temperature of 60°. It was subdivided into 16 ounces; the ounce into 8 drachms. Two pints being = a quart, and 4 quarts = 1 gallon.

The old *ale pint* contained 35·25 cubical inches of water, at 60°.

For chemical use, the most convenient *measure* is the bulk occupied by the troy ounce of distilled water, which may be subdivided into 480 grains, and which is equal to 1·8047 cubical inches.

The IMPERIAL GALLON, now substituted for all other measures of volume, is one-fifth more than the old wine gallon (30 Imperial = 36 Wine), and one-sixtieth less than the old ale gallon (30·5 Imperial = 30 Ale.) It contains 10 avoirdupois pounds of water, of 7000 grains each = 70,000 grains = 277·274 cubic inches of water, at 62°: the weight of the cubic inch of water, at 62°, being 252·458 grains. The IMPERIAL PINT is = one-eighth of the gallon, = 8,750 grains, = 34·66 cubic inches.

1728 cubic inches = 1 cubic foot.

46,656 cubic inches = 27 cubic feet = 1 cubic yard.

1 *bushel* (Imperial) contains 2218·19 cubic inches; and 1 *barrel*, 9981·864 cubic inches.

There are many other units of volume used for particular materials, as the *load* of timber = 50 cubic feet, the *fathom* of firewood =  $6^3 = 216$  cubic feet; and the *rod* of brickwork =  $16\cdot5^2 \times 1\cdot125 = 306\cdot28125$  cubic feet.

### MEASURES OF LENGTH AND SURFACE.

The *inch* is the smallest lineal integer now used. For mechanical purposes it is divided either duodecimally or by continual bisection; but for scientific purposes it is most convenient to divide it decimally. The larger units are thus related to it.

| Mile.   | Furlongs. | Chains. | Rods. | Fathoms. | Yards. | Feet. | Links.            | Inches. |
|---------|-----------|---------|-------|----------|--------|-------|-------------------|---------|
| 1       | =8        | =80     | =320  | =880     | =1760  | =5280 | =8000             | =63360  |
|         | 1         | =10     | =40   | =110     | =220   | =660  | =1000             | =7920   |
|         |           | 1       | =4    | =11      | =22    | =66   | =100              | =792    |
|         |           |         | 1     | =2·75    | =5·5   | =16·5 | =25               | =198    |
|         |           |         |       | 1        | =2     | =6    | =9 $\frac{1}{11}$ | =72     |
|         |           |         |       |          | 1      | =3    | =4 $\frac{6}{11}$ | =36     |
|         |           |         |       |          |        | 1     | =1 $\frac{7}{33}$ | =12     |
| ·000125 | =·001     | =·01    | =·04  | =·11     | =·22   | =0·66 | =1                | =7·92   |



It appears, from the above table, that the *link*, which was invented by Gunter, is expressible in exact decimals of each of the other units, notwithstanding their complex relations. It is difficult to conceive how so large a prime number as 11 could find its way into an artificial system; and its great inconvenience has led, in surveying, to the substitution of the chain and link, (simple decimal parts of the furlong), for the smaller integers in common use.

The English measures of length have been adopted by Russia and Denmark, so that they are now used over the greater part of the world.

The mile, furlong, chain, and link, are applied only to horizontal measures; the fathom is used only for vertical measures, for which also, in levelling, the foot is made the sole unit, and is divided decimally instead of duodecimally. The rod, pole, or perch, is not much used as a lineal measure, but its square is a common superficial measure.

All the units of surface are the squares whose sides = the above units of length, except the three following, which have no corresponding lineal units.

The *rood* = 40 perches = 2·5 square chains = 1210 square yards.

The *acre* = 4 roods = 10 square chains = 4840 square yards.

The *hide* = 100 acres = 1000 square chains = 10 square furlongs.

These superficial measures are used only for land, but the *rod* or *perch* is applied also to walls, while the internal surfaces of buildings are reduced to the *square yard*, and their roofs to an unit called a *square*, consisting of 100 square feet.

For scientific purposes the *square inch* is the most convenient unit of surface. Engineers sometimes use also the *circular inch* = ·7854 &c. of a square inch.

II. FRENCH WEIGHTS AND MEASURES.

THE French metrical system is founded on a single standard of length called a *mètre*, and which is equivalent to the ten-millionth part of the arc of the meridian, extending from the equator to the pole. The length of the *mètre*, as ascertained by Captain Kater, (*Phil. Trans.*, 1818,) is 39·370788 English inches.

The French measures increase and decrease in decimal proportions, a distinctive prefix being put to the term by which the integer is called. These prefixes are *deca*, *hecto*, *kilo*, and *myria*, taken from the Greek numerals, to express the *multiplication* of the integer by 10, 100, 1000, and 10,000 respectively: and *deci*, *centi*, and *milli*, from the Latin numerals, to express the *division* of the integer by 10, 100, or 1000; as in the following table:—

|                    | Metres. |                    | Metre.  |
|--------------------|---------|--------------------|---------|
| 1 Myriamètre ..... | = 10000 | 1 Mètre .....      | = 1·    |
| 1 Kilomètre .....  | = 1000  | 1 Decimètre .....  | = 0·1   |
| 1 Hectomètre ..... | = 100   | 1 Centimètre ..... | = 0·01  |
| 1 Decamètre .....  | = 10    | 1 Millimètre ..... | = 0·001 |

The kilomètre is the general road-measure, and is equal to a mean centesimal minute of the earth's polar circumference. It differs very little from 5 furlongs, English measure.

The *mètre* is the integer of the *measure of length*, and from it all measures of surface, capacity, and weight, are deduced as follows:—

For *superficial dimensions*, the *mètre*, or its parts squared, are employed. When used for measuring land, the term *are* is adopted, which is a decamètre squared, or very nearly 4 perches; so that an *hectare*, or 100 *ares*, is about equal to 2·5 English acres.

For the integer of the *measure of capacity*, the cubed decimètre is employed, under the name of *litre*, which is about equal to  $2\frac{1}{8}$  English wine pints. But for cheap materials, such as firewood, another unit of volume, 1000 times greater than the litre, or equal to a cubic *mètre*, is used, under the name of *stère*, and its multiple and submultiple by 10 constitute a *decastère* and *decistère*.

For the integer of the *measure of weight*, the weight of a cubic centimètre of distilled water, at its maximum density, ( $4\cdot1^{\circ}$  Cent.) weighed *in vacuo*, has been adopted: it is called a *gramme*, and is equal to 15·434 English grains. This unit, however, is obviously too small for the purposes of common life; in which, therefore, its multiple by 1000, or the *kilogramme*, has become the general integer. This weight of pure water occupies exactly a *litre* or cubic decimètre, thus placing the means of verifying the weights, within the reach of every one. The half kilogramme retains the name of the *livre*, though somewhat exceeding the old pound both of France and England; but owing to this excess, the *millier* or 1000 kilogrammes may be taken for all common purposes as = an English *ton*, and the *quintal* or 50 kilogrammes = 1 *cwt.*, a coincidence easily remembered.

The following are the principal tables of French Weights and Measures, which will be found useful in the Laboratory.

| MEASURES OF LENGTH. |   |                 | MEASURES OF VOLUME.       |   |               |
|---------------------|---|-----------------|---------------------------|---|---------------|
|                     |   | English inches. |                           |   | Cubic inches. |
| Millimètre .....    | = | ·03937          | Millilitre .....          | = | ·06103        |
| Centimètre .....    | = | ·39371          | Centilitre .....          | = | ·61028        |
| Decimètre .....     | = | 3·93708         | Decilitre .....           | = | 6·1028        |
| Mètre .....         | = | 39·37079        | Litre .....               | = | 61·028        |
| Decamètre .....     | = | 393·70788       | Decalitre .....           | = | 610·28        |
| Hectomètre.....     | = | 3937·0788       | Hectolitre, or decistère  | = | 6102·8        |
| Kilomètre .....     | = | 39370·788       | Kilolitre, or stère ..... | = | 61028·        |
| Myriamètre.....     | = | 393707·88       | Myrialitre, or decastère  | = | 610280·       |

MEASURES OF WEIGHT.

|                  |   | English grains. |
|------------------|---|-----------------|
| Milligramme .... | = | ·0154           |
| Centigramme .... | = | ·1543           |
| Decigramme ....  | = | 1·5434          |
| Gramme .....     | = | 15·434          |
| Decagramme ....  | = | 154·34          |
| Hectogramme....  | = | 1543·4          |
| Kilogramme ....  | = | 15434·          |
| Myriagramme....  | = | 154340·         |



The *kilogramme* is  $= 2.68098$  pounds troy; or  $2.20606$  pounds avoir-du-pois.

The *coins* also are made to bear simple relations both to these weights and to the measures; for the *franc* weighs 5 grammes; the *five-franc* piece, 25 grammes; and its diameter  $= 37$  millimètres, so that 27 of them, side by side, measure a mètre;  $37 \times 27 = 999$ .

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